

PHASE SPACE FORMULATION OF THE QUANTUM MANY-BODY PROBLEM

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## ABSTRACT

By means of a quantum mechanical phase space distribution function introduced by von Roos, the Schroedinger equation for a non-relativistic system of  $N$  identical particles with scalar interactions is transformed into a quantum mechanical generalization of the Liouville equation, thereby formulating the problem in terms of a generalized density in phase space, a quantity of primary interest in most treatments of the corresponding classical system (or "plasma"). This transformation permits a parallel development of the theories of classical and quantum plasmas and thus allows the quantum many-body problem to be discussed virtually completely in classical terms. In particular, a kinetic theory of quantum plasmas is obtained by deriving the quantum analogue of the BBGKY hierarchy, and applying thereto approximation techniques similar to those of Rostocker and Rosenbluth, and Bogoliubov. The point of departure from similar previous studies based on the Wigner distribution function is that the proper exchange symmetry can be tractably introduced into the formalism.

Attention is first focused on the Hartree and Hartree-Fock approximations, in which case the quantum BBGKY system reduces to a simple quantum generalization of the Vlasov equation. This equation is used to study the response of spatially homogeneous systems to weak external forces, and the associated problems of plasmon and spin-wave excitations. It is also used to derive the quantum and exchange corrected equations of inviscid hydrodynamical transport which are then applied to the problem of sound propagation in the degenerate electron gas.

The second part of the study is concerned with the theory of the many-electron atom in the Hartree and Hartree-Fock approximations.

The relevant quantum Vlasov equations lead naturally to a "statistical" theory of the atom which reduces to the Thomas-Fermi-Amaldi and Thomas-Fermi models (respectively) as  $\hbar \rightarrow 0$ . For  $\hbar \neq 0$ , the quantum and exchange corrections to these models are simultaneously generated. The quantum hydrodynamical theory developed earlier is used to determine the influence of these corrections on the boundary conditions of the model, and a theory of the compressed atom is consequently obtained. Considered in somewhat less detail are the effects of non-zero temperature, net orbital angular momentum, relativity and correlations, as well as time dependent processes.

The final part deals with the problem of the degenerate electron gas with a uniform neutralizing background. Going beyond the Hartree-Fock approximation, the pair correlation functions for particles with "parallel" and "anti-parallel" spin are obtained by neglecting three-particle correlations. From these functions, a quantum-mechanical collision integral is derived which differs from that obtained by Silin and Guernsey and conjectured by Wyld and Pines in that dynamical exchange effects are included. Also obtained from the pair correlation function is an expression for the "correlation energy" which reduces in the high density limit to the result of Gell-Mann and Brueckner. At intermediate densities an additional term appears in the energy due to the screening of the exchange interaction by the dielectric properties of the medium. It is evaluated in the high density limit and found to be  $-0.151 r_s \ln r_s$  Ryd/electron in marked disagreement with the corresponding value obtained by DuBois.

## TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. GENERAL THEORY	
A. Statement of Problem	9
B. Outline of Classical Approach	10
C. Quantum Liouville Equation	25
D. Quantum BBGKY Hierarchy	40
III. THE STATISTICAL HARTREE APPROXIMATION	
A. General Remarks	47
B. First Quantum Vlasov Equation	49
C. Response of Spatially Uniform System to Weak External Forces	53
D. Quantum Hydrodynamics	58
IV. THE HARTREE-FOCK APPROXIMATION	
A. General Remarks	69
B. Second Quantum Vlasov Equation	82
C. Spatially Homogeneous Systems	88
D. Quantum Hydrodynamics	99
V. PLASMA THEORY OF THE MANY-ELECTRON ATOM	
A. Introduction and Background	111
B. Derivation of Model	119
C. Theory of the Compressed Atom	132
D. Perturbation Technique for Approximate Solution of Model	137

V.	E.	Application of Method to Other Problems	141
	F.	Non-Equilibrium Processes and Excited States	143
	G.	Relativistic and Correlation Corrections	148
VI.		CORRELATIONS AND COLLISIONS IN THE UNIFORM ELECTRON GAS	
	A.	Introduction	154
	B.	Solution for the Pair Correlation Function	158
	C.	The Collision Integral	172
	D.	The Correlation Energy	183
VII.		SUMMARY AND CONCLUSIONS	200
		References	204
		Appendix A - Reprint of Paper "Plasma Theory of the Many-Electron Atom", by P. H. Levine and O. von Roos	207
		Appendix B - Solution of Exchange-Corrected Energy Transport Equation	214
		Appendix C - Solution of Time-Independent Quantum Vlasov Equation to Order $\hbar^2$	217

## I. Introduction

The classical and quantum approaches to the many-body problem have undergone considerable refinement in recent years, along markedly different lines and at the consequent expense of an ever-widening conceptual gap between the two. The former, under the impetus of the increasing technological importance of "plasmas", has concerned itself largely with a detailed understanding of the physical consequences of the Liouville equation, which describes the temporal evolution of the distribution in phase space of the members of a representative ensemble and embodies therein both equilibrium and non-equilibrium statistical mechanics and transport theory. The latter, on the other hand, has tended to follow the development of quantum theory as a whole, beginning with the density matrix formulation of quantum statistical mechanics due to von Neumann (1) and Dirac (2) and eventually adopting the full arsenal of quantum field theory (see e.g. DeWitt (3)) as the formal similarity between certain many-body problems and field theory came to be appreciated. Indeed, Nambu's (4) recent proposal that the masses of elementary particles arise in a manner similar to that of the energy gap in the B.C.S. theory of superconductivity emphasizes both the closeness and symbiotic nature of the present connection between field theory and the quantum many-body problem.

An unfortunate concomitant of the undeniable power and formal elegance of such field theoretic approaches to the many-body problem, however, is the obscurity with which the correspondence principle is

cloaked by the formalism. Even the density matrix approach, which bears a strong resemblance at many points to the classical theory, suffers in this regard. This characteristic feature is more than merely a pedagogic drawback for two reasons. First, there exist in nature many-body systems which are "quasi-classical" in the sense that the difference between quantum and classical equations of motion and/or statistics only slightly influences certain properties of the system and hence can be treated as a small perturbation in their calculation. For example, the transport properties of a weakly degenerate interacting gas and (as we shall find) certain gross features of many-electron atoms fall into this category. To determine quantum and exchange\* corrections to the classical theory in such cases, one must be able to go to the correspondence limit of the quantum many-body theory. A second, and perhaps more compelling reason follows from the realization that even in intrinsically quantum-mechanical many-body systems far from the correspondence limit, the essential theoretical difficulties often arise not from quantum mechanics, but rather from the fact that a large number of interacting particles are involved - the very same essential difficulty faced by the plasma theorist in his studies of classical systems. Consequently, the lack of a clear cut path (and common conceptual framework) between the classical and quantum

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\*Throughout this work, we shall designate effects arising from the difference between quantum-mechanical and classical equations of motion as "quantum" effects. "Exchange" effects refer to the consequences arising from the symmetry properties of the wave function under particle interchange.



many-body theories precludes the ready adaptation to the latter of new techniques and insights gained from a study of the classical problem. For example, an approximation procedure based on the quantum analogue of the Rostocker-Rosenbluth (5) and Bogoliubov (6) treatments of the Liouville equation may be more convenient in dealing with some aspects of the electron-gas problem than the Rayleigh-Schroedinger perturbation theory (with or without diagrammatic aids) or the "random phase" approximation - a question we will come to examine in some detail.

If the gap is to be bridged (and there seems good reason to do so), what clearly is needed is a new formulation of the quantum many-body problem, one based not on the density matrix, Green's functions or second quantization, but rather upon a quantum-mechanical generalization of the phase space density which underlies the classical theory. To accomplish this, a quantum-mechanical phase space distribution function (q.m.d.f.) must be defined in terms of the N-body wavefunctions of a representative ensemble, and its dynamical equation obtained from the Schroedinger equation. The q.m.d.f. so chosen must not only be a normalizable c-number from which information is obtained in the same fashion as with classical distribution functions (its lack of positive definiteness and observability notwithstanding), but its dynamical equation must go over to the Liouville equation when  $\hbar$  is formally set equal to zero, thereby guaranteeing the correct correspondence limit.

The first search for such a function was made by Wigner (7) in 1932. He found that in fact many q.m.d.f.'s with the desired properties

could be defined, the choice among them to be determined largely from the standpoint of convenience. His choice, the so-called Wigner distribution function has been almost exclusively used since then (we will exhibit it later). With it, Wigner calculated lowest order quantum corrections to the classical Boltzmann equation. It has also been applied extensively by Kirkwood and collaborators (8) in deriving transport equations for low density gases and to formulate a hydrodynamics of quantum fluids. Saenz (9) also derived a transport equation for a dilute, non-degenerate, spinless gas using this function.

Extensive development of the theory based on the Wigner function was retarded, however, by two circumstances (probably accounting for the relatively minor role of q.m.d.f.'s in contemporary quantum many-body physics). First, full exploration of the strictly classical system of many interacting particles has only relatively recently been undertaken, under the banner of "plasma" physics (5,6). Consequently, a detailed understanding of the properties of q.m.d.f.'s had to await corresponding advances in the classical theory. A more fundamental difficulty, however, arose from the analytic complexity of the equation for the Wigner function in the Hartree-Fock approximation. This inability of the Wigner function to tractably incorporate the proper exchange symmetry of the wave function effectively limited its usefulness to the Hartree approximation, a severe restriction in many practical applications.

The way out of this latter difficulty was found in 1960 by von Roos (10) (independently of an earlier, more cursory observation by



Takabayasi (11)) who, pursuing Wigner's observation that many alternative q.m.d.f.'s with the desired properties could be defined, examined such possibilities in the hope that with one of them, exchange could be introduced in a more natural and tractable fashion than with the Wigner function. His efforts were successful and enabled him to derive a quantum-mechanical generalization of the collisionless-Boltzmann (Vlasov) equation from the Hartree-Fock equations. In a series of papers, this formalism was used to derive lowest order quantum and exchange corrections to the plasmon dispersion relation in low density non-degenerate plasmas (12), the high density electron gas (13), and the electron-phonon system (14). An indication that the formalism could be fruitfully applied to the time-independent equilibrium properties of finite systems as well was given in 1962 by the Author and von Roos (15) (see Appendix A) in a paper which established the theoretical foundations of the Thomas-Fermi statistical model of the atom from the Hartree-Fock equations and succeeded in deriving quantum and exchange corrections to this model. This paper forms the nucleus for part of this dissertation.

Thus, the two obstacles which formerly stood in the way of a q.m.d.f. approach to the quantum many-body problem are no longer present. Recent developments in plasma physics (notably the application of the techniques due to Bogoliubov (6), Born and Green (16), Kirkwood and collaborators (8) and Yvon (17) to a classical plasma with Coulomb interactions by Rosenbluth and Rostocker (5) ) have yielded insights into the properties of distribution functions in the corresponding classical problem and serve as a guide for a parallel development in terms of the

q.m.d.f. Furthermore, use of the von Roos q.m.d.f. in place of the Wigner function will allow the proper exchange symmetry to be introduced in a tractable fashion. The primary purpose of this dissertation is to carry out this development and to investigate what types of physical situations can be effectively studied by such a formalism. In the course of this program, we will refine and extend von Roos' original somewhat awkward formulation (compare, for example, our equation IV-64 with equation 29) of reference 10) and will find that the method has relevance not only to quasi-classical problems, but such intrinsically quantum systems as the degenerate electron gas as well, leading us to believe that the formalism may be applicable to a broader class of problems than might be inferred from the specific examples herein considered.

In Chapter II, after a more complete definition of the problem and an outline of the classical many-body (plasma) theory which is to serve as a general guide to the development of the quantum many-body theory, we introduce the von Roos q.m.d.f. and derive the quantum Liouville equation, as well as the consequent analog of the BBGKY hierarchy of coupled equations for the "reduced" q.m.d.f.'s. As in the classical case, this hierarchy is approached by successive truncations of the chain, corresponding to the inclusion of dynamical correlations (or "collisions") between a successively greater number of particles.

The first step in this procedure, corresponding to the Hartree approximation to the N-body wave function, is carried out in Chapter III.

In this case, the quantum B. B. G. K. Y. hierarchy reduces to a simple generalization of the Vlasov equation which is used to study the response of a spatially homogeneous system to weak external forces. Singularities in the response function are identified with "plasmons" and their dispersion relation is obtained. Velocity space moments of the quantum Vlasov equation are then taken and yield the equations of inviscid, isentropic quantum hydrodynamics.

In Chapter IV, the Hartree-Fock approximation is introduced and is found to be formally equivalent to a second generalization of the Vlasov equation, by means of which the spatially homogeneous electron gas at non-zero temperatures is studied in some detail. Its response to weak external fields is again investigated, and the exchange-corrected plasmon equation is derived. A new mode of excitation, the spin wave, appears naturally in the theory and its dispersion relation is obtained. The quantum hydrodynamical theory of Chapter III is re-derived and corrected for exchange effects. As an application, sound propagation in a degenerate electron gas is studied, and we find that due to exchange, a critical temperature exists (at any density) such that sound waves cannot propagate at temperatures below this value.

The formal equivalence between the Hartree-Fock equations and the quantum Vlasov equation motivates the "plasma theory of the many-electron atom" presented in Chapter V, by means of which the theoretical foundations of the Thomas-Fermi, Thomas-Fermi-Dirac and Fermi-Amaldi statistical atomic models are investigated in some detail. Quantum,

exchange and non-zero temperature corrections are derived, and the theory of the compressed atom is similarly corrected using the quantum hydrodynamical analysis of Chapter IV. Excitations of the atom are studied, and we are led to anticipate the existence of "collisionless" modes of collective oscillation, the equations for which are presented but not solved. Corrections to the model due to relativity and correlations are also briefly discussed.

In Chapter VI, the first step beyond the Hartree-Fock approximation is taken by introducing dynamical two-particle correlations into the theory. The consequent equations represent the starting point for an exact kinetic theory of quantum plasmas, paralleling recent work by Guernsey (18) which, being based on the Wigner distribution function, does not properly include exchange effects. The particular example of the spatially uniform electron gas is studied, and the "parallel" and "anti-parallel" spin pair correlation functions are obtained. From them we derive a new quantum-mechanical collision integral which, in the absence of dynamical exchange effects, reduces to that recently conjectured and studied by Wyld and Pines (19). Finally, we also obtain from the pair correlation functions an expression for the interaction energy of the electron gas which, when combined with the Pauli-Feynman theorem, yields the "correlation energy". At zero temperature, the equivalence of this expression in the high density limit with the Gell-Mann-Brueckner result is explicitly demonstrated. At intermediate densities, a new term in the energy appears due to the screening of the

exchange interaction by the dielectric behavior of the medium which, when numerically evaluated in the high density limit, is in disagreement with the result obtained by DuBois (92).



## II. General Theory

### A. Statement of Problem

In its full generality, the many-body problem may be defined as that of obtaining a physical description of the observable properties of a system of  $N$  objects, proceeding from a knowledge of the nature of the interaction between the objects, their equations of motion and a detailed understanding of the properties of each when isolated in vacuo. The system may be exposed to external influences of a prescribed or statistical nature, but these do not represent an additional degree of freedom, i.e. they are not affected by the behaviour of the objects comprising the system. The classical and quantum problems are distinguished both by different "equations of motion" and, more fundamentally, by the different interpretations which must be given to the phrase "observable properties".

For the purposes of this dissertation, we shall be dealing with a far more restricted many-body problem, although the lines along which the theory can be extended to more general situations will be apparent. Specifically, we shall assume that the  $N$  particles are: identical, possess no internal structure or degrees of freedom other than spin, interact with each other and with external objects through superposable forces derivable from a scalar potential, and obey non-relativistic equations of motion (i.e. the Schroedinger equation). We might remark parenthetically that all of these restrictions save the last are made purely for convenience and do not represent essential limitations of the theory. Finally, we assume that the system is not "solid-like" in the sense that

the  $N$  particles are more or less localizable on fixed lattice sites - a case which must be studied by methods entirely different from those we are about to describe.

### B. Outline of Classical Approach

The classical theory begins with a consideration not of a single  $N$ -body system with fully prescribed initial conditions on the  $6N$  generalized coordinates and momenta, but rather with a representative ensemble of macroscopically similar systems each described by the same Hamiltonian. Appeal is made to the quasi-ergodic hypothesis which states that the statistical properties of measurements of some quantity  $Q$  performed on a single system can be inferred to an arbitrary degree of accuracy from the distribution of the values of  $Q$  among the members of the ensemble, simply by choosing a large enough representative ensemble. Choosing the generalized coordinates to be the location ( $\underline{x}$ ) in a Cartesian configuration space, and the generalized momenta to be the linear momenta ( $\underline{p}$ ), a  $6N$  dimensional phase space ( $\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N$ ) is introduced, each system being represented at a given time by a point in this space. The normalized distribution of system points in phase space at a given time,  $F^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N; t)$  is defined and its dynamical equation, the so-called Liouville equation, is obtained from the Newtonian

equations of motion. It can be written in the form ( $\mathcal{L}^{(N)}$  being the N-particle Liouville operator):

$$\mathcal{L}^{(N)} F^{(N)} \equiv \frac{\partial F^{(N)}}{\partial t} + \left\{ F^{(N)}, H^{(N)} \right\}_{\text{P.B.}}^{(N)} = 0 \quad (\text{II-1})$$

where the N-particle Poisson bracket of  $F^{(N)}$  with the Hamiltonian  $H^{(N)}$  is defined by

$$\left\{ F^{(N)}, H^{(N)} \right\}_{\text{P.B.}}^{(N)} \equiv \sum_{i=1}^N \left( \nabla_{\underline{x}_i} F^{(N)} \cdot \nabla_{\underline{p}_i} H^{(N)} - \nabla_{\underline{p}_i} F^{(N)} \cdot \nabla_{\underline{x}_i} H^{(N)} \right) \quad (\text{II-2})$$

In conformity with the remarks of the previous section, the N-body Hamiltonian is chosen as

$$H^{(N)} = \sum_{i=1}^N \left[ \frac{|\underline{p}_i|^2}{2m} + \frac{g^2}{2} \sum_{\substack{j=1 \\ j \neq i}}^N \phi(\underline{x}_i - \underline{x}_j) + g^2 \phi^{\text{ext}}(\underline{x}_i, t) \right] \quad (\text{II-3})$$

where  $g^2 \phi(\underline{x}_i - \underline{x}_j)$  is the scalar potential of interaction between particles  $i$  and  $j$ ,  $g^2 \phi^{\text{ext}}$  is the external potential and  $g^2$  the "coupling constant" which characterizes the strength of the interaction. The system of equations is completed by a normalization condition which may be chosen as

$$\int d^3x_1 \dots d^3x_N d^3p_1 \dots d^3p_N \bar{F}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, \underline{p}_1, \dots, \underline{p}_N; t) = 1 \quad (\text{II-4})$$



The ensemble average  $\bar{\Gamma}^{(N)}(t)$  of any function  $G^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N)$  at a time  $t$  is determined by direct integration with  $F^{(N)}(t)$  over phase space:

$$\bar{\Gamma}^{(N)}(t) = \int d^3x_1 \dots d^3x_N d^3p_1 \dots d^3p_N G^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N) F^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N; t) \quad (\text{II-5})$$

and, by the ergodic hypothesis, is identified with the expected value of a measurement of  $G^{(N)}$  performed on any member of the ensemble at time  $t$ .

Two subsidiary restrictions on  $F^{(N)}$  must be noted. First, because it is a distribution function, it must be positive semi-definite, i.e.

$$F^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_N; t) \geq 0 \quad (\text{II-6})$$

Second, due to the assumed identity of the  $N$  particles,  $F^{(N)}$  must be symmetric under the interchange of any two of them. This is actually a statement about the properties of the representative ensemble chosen, since classically the particles though identical are distinguishable. Thus

$$\begin{aligned} F^{(N)}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_i, \dots, \underline{p}_j, \dots, \underline{p}_N; t) \\ = F^{(N)}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{p}_1, \dots, \underline{p}_j, \dots, \underline{p}_i, \dots, \underline{p}_N; t) \end{aligned} \quad (\text{II-7})$$

By means of this relation, we can illustrate the fact that the full  $F^{(N)}$  contains much more information than is practically required. For example,

if we wish to compute the average kinetic energy  $\overline{T^{(N)}}$  of the system, we set  $G^{(N)}$  in II-5 equal to  $\sum_{i=1}^N \frac{|p_i|^2}{2m}$  and by repeated use of II-7 find

$$\overline{T^{(N)}} = N \int d^3x, d^3p, \frac{|p_i|^2}{2m} \left\{ \int d^3x_2 \cdots d^3x_N d^3p_2 \cdots d^3p_N F^{(N)}(x_1, \dots, x_N, p_1, \dots, p_N; t) \right\} \quad (\text{II-8})$$

Similarly, the average interaction energy  $\overline{V^{(N)}}$  is obtained by choosing  $G^{(N)}$  equal to  $\left[ \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N g^2 \phi(x_i - x_j) + \sum_{i=1}^N g^2 \phi^{\text{ext}}(x_i) \right]$  yielding

$$\begin{aligned} \overline{V^{(N)}} = & \frac{N(N-1)}{2} g^2 \int d^3x, d^3x_2 d^3p, d^3p_2 \phi(x_1 - x_2) \left\{ \int d^3x_3 \cdots d^3x_N d^3p_3 \cdots d^3p_N F^{(N)} \right\} \\ & + N g^2 \int d^3x, d^3p, \phi^{\text{ext}}(x_1, t) \left\{ \int d^3x_2 \cdots d^3x_N d^3p_2 \cdots d^3p_N F^{(N)} \right\} \end{aligned} \quad (\text{II-9})$$

Thus, all one requires to compute the average system energy, for example, are the so-called "reduced" distribution functions enclosed in curly brackets. This is the motivation for dealing not with the full Liouville equation II-1 but rather with a hierarchy of coupled equations for reduced distribution functions (the so-called BBGKY hierarchy) obtained by integrating II-1 over sub-spaces of the full phase space. Specifically, if we define the s-particle reduced distribution functions

$$F_N^{(s)}(x_1, \dots, x_s; p_1, \dots, p_s; t) \equiv \int d^3x_{s+1} \cdots d^3x_N d^3p_{s+1} \cdots d^3p_N F^{(N)}(x_1, \dots, x_N, p_1, \dots, p_N; t) \quad (\text{II-10})$$

then one obtains from II-1, the set of N-1 coupled equations

$$\mathcal{L}^{(S)} F_N^{(S)} \equiv \frac{\partial F_N^{(S)}}{\partial t} + \left\{ F_N^{(S)}, H^{(S)} \right\}_{p.B.}^{(S)} = (N-S) g^2 \sum_{i=1}^S \int d^3 x_{S+1} d^3 p_{S+1} \left[ \nabla_{\tilde{x}_i} F_N^{(S+1)} \cdot \nabla_{\tilde{x}_i} \phi(\tilde{x}_i - \tilde{x}_{S+1}) \right] \quad (\text{II-11})$$

It is readily verified that  $F_N^{(S)}$  has the same symmetry property (II-7) and normalization (II-4) as the full  $F^{(N)}$ .

The problem now becomes one of developing a suitable approximation scheme to apply to (II-11). The most fruitful one is suggested by our previous observation that a good deal of information is contained in just  $F_N^{(1)}$  and  $F_N^{(2)}$ , or more generally speaking, that the information content of  $F_N^{(S+1)}$  not present in  $F_N^{(S)}$  concerns increasingly finer details of the system as (S) increases. Since such details are generally neither of much theoretical interest nor amenable to experimental study, one is led to consider successive truncations of the hierarchy (II-11). Specifically, one begins by considering only the first equation of II-11 (i.e. (S) = 1) which connects  $F^{(1)}$  with  $F^{(2)}$ . The resulting equation

$$\begin{aligned} \frac{\partial F_N^{(1)}}{\partial t} + \nabla_{\tilde{x}_1} F_N^{(1)} \cdot \frac{\tilde{p}_1}{m} - \nabla_{\tilde{p}_1} F_N^{(1)} \cdot \nabla_{\tilde{x}_1} g^2 \phi^{ext}(\tilde{x}_1, t) \\ = (N-1) g^2 \int d^3 x_2 d^3 p_2 \left[ \nabla_{\tilde{p}_1} F_N^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{p}_1, \tilde{p}_2; t) \cdot \nabla_{\tilde{x}_1} \phi(\tilde{x}_1 - \tilde{x}_2) \right] \end{aligned} \quad (\text{II-12})$$

is then closed by the ansatz

$$F_N^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{p}_1, \tilde{p}_2; t) = F_N^{(1)}(\tilde{x}_1, \tilde{p}_1; t) F_N^{(1)}(\tilde{x}_2, \tilde{p}_2; t) \quad (\text{II-13})$$

and the consequent properties of  $F_N^{(1)}$  are studied. The next step is the retention of the first two equations of II-11 ( $S = 1, 2$ ) with (II-13) replaced by

$$F_N^{(3)}(\tilde{x}_1, \tilde{x}_2, \tilde{x}_3; \tilde{p}_1, \tilde{p}_2, \tilde{p}_3; t) = \left[ F_N^{(1)}(\tilde{x}_1, \tilde{p}_1) F_N^{(2)}(\tilde{x}_2, \tilde{x}_3; \tilde{p}_2, \tilde{p}_3; t) + \left\{ \text{cyclic permutation of } 1, 2, 3 \right\} \right] \times \text{normalization constant} \quad (\text{II-14})$$

yielding coupled equations for  $F_N^{(1)}$  and  $F_N^{(2)}$  which are usually solved by assuming that  $F_N^{(1)}$  will differ only slightly in this case from the  $F_N^{(1)}$  obtained in the first step so that perturbation theory can be used. One then, in principle, considers ( $S = 1, 2, 3$ ) and so forth.

When this procedure is carried beyond ( $S = 1$ ), formidable mathematical difficulties arise in the general case, and additional approximations are required. What one does is to rewrite the equations in terms of dimensionless parameters appropriate to the problem at hand and then develop therefrom a perturbation series in such parameters. This generally enables one to ignore troublesome terms in the lowest order. The Rostocker-Rosenbluth (5) procedure and Mayer "cluster expansion" (20) may be cited as examples. We do not wish to discuss such parametrization procedures here beyond the remark that invariably the expansion parameter is related to the ratio of the average interaction energy to the average kinetic energy.

In spite of the foregoing simplifications, the method has enormous power. Consider, for example, the first step of the procedure.



Combining II-12 and II-13, one obtains for  $F_N^{(1)}$  the equation

$$\frac{\partial F_N^{(1)}}{\partial t} + \nabla_{\tilde{x}_1} F_N^{(1)} \cdot \frac{\tilde{p}_1}{m} - \nabla_{\tilde{p}_1} F_N^{(1)} \cdot \nabla_{\tilde{x}_1} g^2 (\phi^{\text{ext}}(\tilde{x}_1, t) + \phi^{\text{s.c.F.}}(\tilde{x}_1, t)) = 0 \quad (\text{II-15})$$

where the "self-consistent field"  $\phi^{\text{s.c.F.}}$  is given by

$$\phi^{\text{s.c.F.}}(\tilde{x}_1, t) \equiv (N-1) \int d^3 \tilde{x}_2 d^3 \tilde{p}_2 F_N^{(1)}(\tilde{x}_2, \tilde{p}_2, t) \phi(\tilde{x}_1 - \tilde{x}_2) \quad (\text{II-16})$$

This can be written in more familiar form by noting that the average particle density,  $\rho(\tilde{x}, t)$ , is given by

$$\rho(\tilde{x}, t) = N \int d^3 p F_N^{(1)}(\tilde{x}, \tilde{p}, t) \quad (\text{II-17})$$

so that II-16 becomes

$$\phi^{\text{s.c.F.}}(\tilde{x}_1, t) = \frac{N-1}{N} \int d^3 \tilde{x}_2 \rho(\tilde{x}_2, t) \phi(\tilde{x}_1 - \tilde{x}_2) \quad (\text{II-18})$$

Equation II-15, known as the collisionless-Boltzmann or Vlasov equation for reasons to be discussed presently, is of fundamental importance both to equilibrium statistical mechanics and to studies of the collective behavior of classical plasmas. Let us explore this point in more detail.

An N-body system not subjected to time varying external forces is said to be in statistical equilibrium if it can be described by a time-independent (or "stationary") representative ensemble, i.e.  $\frac{\partial F_N^{(s)}}{\partial t} = 0$ . Setting the first term of II-15 equal to zero and solving the resulting equation, one finds the most general solution to be any functional of the constants of the motion of a single particle in the field described by  $g^2(\phi^{\text{ext}} + \phi^{\text{S.C.F.}})$ , among which is the energy

$$e = \frac{p^2}{2m} + g^2(\phi^{\text{ext}} + \phi^{\text{S.C.F.}}) \quad (\text{II-19})$$

Hence any  $F_N^{(1)} = f(e)$  will constitute a stationary solution, but the theory at this stage of approximation does not indicate what functional dependence to choose, except in the special situation where we are describing an isolated conservative system. In this case one chooses the so-called microcanonical ensemble defined by

$$f(e) = \text{const} \times \delta(e - e_0) \quad (\text{II-20})$$

$\delta$  being the Dirac delta function. Of far greater importance are systems in equilibrium with a thermostat at temperature T. To determine  $f(e)$  in this case, the most direct procedure would be to simply require that the proper choice is that which reproduces the (macroscopic) laws of thermodynamics. Indeed, one finds that this can be achieved with the so-called macrocanonical ensemble

$$f(e) = \exp\left[\frac{\psi - e}{kT}\right] \quad (\text{II-21})$$

which correctly describes the macroscopic behavior of a system in thermal equilibrium at temperature T.\*

Instead of ensemble theory, one can follow the microscopic kinetic approach due to Boltzmann. In a sense this tries to anticipate the result of carrying out the second step of the approximation (i.e. II-14). Since the ansatz II-13 is tantamount to the neglect of particle collisions (each particle feeling only the average self-consistent field), II-14 will introduce collisions into the theory. Specifically, to II-15 will be added a term which describes the rate of change of  $F_N^{(1)}$  due to fluctuations about this self-consistent field (which is what one means by collisions) so that we formally anticipate II-15 to be replaced by

$$\frac{\partial F_N^{(1)}}{\partial t} + \nabla_{\underline{x}_1} F_N^{(1)} \cdot \frac{\underline{p}_1}{m} - \nabla_{\underline{p}_1} F_N^{(1)} \cdot \nabla_{\underline{x}_1} g^2(\phi^{\text{ext}}(\underline{x}_1, t) + \phi^{\text{S.C.F.}}(\underline{x}_1, t)) = \frac{\partial F_N^{(1)}}{\partial t} \Bigg|_{\text{collisions}} \quad (\text{II-22})$$

Since collisions are the mechanism by which thermal equilibrium is established, the proper choice for  $f(e)$  is that which makes the right hand side of II-16 vanish. From a detailed consideration of the two-body elastic collision process, Boltzmann obtained an expression for

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\*  $\psi$  will in general be a function of the remaining constants of the motion.

for  $\frac{\partial F_N^{(0)}}{\partial t}$  collisions, the so-called collision integral,\* which in fact is found to vanish for the unique choice II-21. Alternatively, one can exploit Boltzmann's observation that by virtue of two-body collisions, the quantity H defined by

$$H(t) \equiv \int d^3x, d^3p, (\ln F_N^{(0)}) F_N^{(0)}(x, p, t) \quad (\text{II-22})$$

never increases, and that equilibrium is reached when H attains its minimum value.. Applying the variational calculus to the consequent relation

$$\delta H / \delta F = 0 \quad (\text{II-23})$$

leads again to the "Maxwell-Boltzmann" distribution II-21. We see, therefore, that II-15 in conjunction with either thermodynamics and ensemble theory or the H theorem will yield classical equilibrium statistical mechanics. We shall see presently that in going to the next step (i.e. II-14), such outside appeals will no longer be necessary to achieve this result. First, however, we wish to point out that the utility of II-15 extends beyond equilibrium statistical mechanics: implicitly time-dependent phenomena can be described by this equation in two limiting cases. At one extreme, the response of the system,

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\*When this expression is introduced into II-16, the resulting relation is known as the Boltzmann equation. The reason for calling II-15 a "collisionless" Boltzmann equation is apparent.



initially in thermal equilibrium, to a  $\phi^{\text{ext}}$  which is switched on at  $t = 0$  and varies in time at a rate large compared to the thermal relaxation time (or "collision frequency") will be obtainable for early times from this equation. This is equivalent to saying that when collisions don't have time to act, they can be ignored. As a corollary, for certain systems characterized by long-range interparticle forces II-15 is useful in studying collective excitations mediated by these forces when the excitation frequency is large compared to the collision frequency, as pointed out by Vlasov (21) in his treatment of coulomb plasmas.

At the opposite extreme, the response of the system to external forces that vary at a rate slow compared to the collision frequency is also described by II-15 since in this case, the system is in quasi-static equilibrium, i.e. it can be viewed as passing continuously from one equilibrium state to another. This is what one may call the hydrodynamic limit. Indeed, by taking the first three moments of II-15 in velocity space, the continuity equations for mass, momentum and energy are obtained. Then assumption of local thermodynamic equilibrium is introduced by taking  $F_N^{(1)}(\underline{x}, t)$  to be given by II-21, where  $\psi$  and  $T$  are now permitted to vary in space and time. Since II-15 contains no mechanism for dissipation, we obtain in this fashion the equations of compressible inviscid hydrodynamics. Viscosity (or, analogously, resistivity when we deal with a system of charges) can of course be introduced in a phenomenological fashion. To generate these so-called transport coefficients from the theory itself, one must go to the second step of the approximation

procedure, II-14.

There are, naturally, more compelling reasons for going to the next step. Recall first that from II-9, the average interaction energy is determined from  $F_N^{(2)}$ ; corrections to  $F_N^{(2)}$  generated by II-14 will thus influence this energy and, as a consequence, the equation of state of the system (i.e. the Virial coefficients). Secondly, we wish to obtain the collision integral, not only to verify that the H theorem holds and that equilibrium statistical mechanics is indeed contained in the theory, but also so that non-equilibrium processes can be studied. In particular, such questions as the approach to equilibrium of a system prepared in an arbitrary initial state, and the influence of collisions on collective excitations can now be answered within the context implied by II-14, viz, that only two-body collisions (or "correlations") are considered.

The program implicit in the second step may be described as follows. With ansatz II-14, the ( $S = 2$ ) equation in II-11 will, when solved, determine  $F_N^{(2)}$  in terms of  $F_N^{(1)}$ . The  $F_N^{(2)}$  thus derived is then inserted into the ( $S = 1$ ) equation which is now closed. Equilibrium is established when the right hand side (the "collision integral") of this equation vanishes, a condition which determines the equilibrium value of  $F_N^{(2)}$  which, together with  $F_N^{(1)}$  equil., gives the energy (through II-8 and II-9). Non-equilibrium processes are studied by means of the full, time-dependent,  $F_N^{(1)}$  equation.

In attempting to carry out this program, two difficulties arise. The first is due to the analytic complexity of the ( $S = 2$ ) equation,

necessitating a perturbation expansion in some small dimensionless parameter as mentioned earlier. The second is more fundamental, being related to the question of how the Liouville equation which is derived from the time reversible equations of motion can yield the time irreversible equations demanded by statistical mechanics. The usual procedure is to accept only those solutions which asymptotically become constant in time as  $t \rightarrow \infty$ , rejecting other solutions as "unphysical". In Green's function language, one chooses the "retarded" Green's function. In addition, one generally introduces Bogoliubov's (6) concept of a hierarchy of relaxation times. This is based on the assumption that the characteristic times ( $\tau_s$ ) in which the various  $F_N^{(s)}$  approach their asymptotic values become progressively shorter as (s) increases. Consequently, for times long compared to  $\tau_s$ , the time dependence of  $F_N^{(s)}$  is assumed to arise only implicitly through the time dependence of  $F_N^{(s-1)}$ . Within these restrictions, the program has been carried out for the special case of a spatially uniform plasma with Coulomb interactions by Rostocker and Rosenbluth (5), Balescu (22), Lenard (23), and Guernsey (24). They find for the collision integral an expression which may be written as (to within a normalizing constant):

$$\left. \frac{\partial F_N^{(1)}(\underline{p}_1)}{\partial t} \right|_{\text{Collisions}} = \text{const.} \times \nabla_{\underline{p}_1} \cdot \int d^3 \underline{p}_2 \left\{ \int \frac{d^3 \underline{q}}{q^4} \underline{q} \underline{q} \frac{\delta(\underline{q} \cdot (\underline{p}_1 - \underline{p}_2))}{|K(\underline{q}, \underline{q}, \underline{p}_1)|^2} \right\} \quad (\text{II-24})$$

$$\cdot \left\{ \left( \nabla_{\underline{p}_1} F_N^{(1)}(\underline{p}_1) \right) F_N^{(1)}(\underline{p}_2) - F_N^{(1)}(\underline{p}_1) \left( \nabla_{\underline{p}_2} F_N^{(1)}(\underline{p}_2) \right) \right\}$$



This is identically zero for the unique non-trivial choice (II-21) as anticipated. It differs from the collision integral proposed by Boltzmann, however, in that the collision cross-section (first curly bracket) contains the dynamic dielectric constant of the medium,  $K$ , defined by

$$\chi(\underline{q}, \omega) = 1 + \left( \text{normalization constant} \right) \frac{\omega_p^2}{q^2} \int d^3p \frac{\underline{q} \cdot \nabla_p F_N^{(1)}(p)}{\omega + i\eta - \underline{q} \cdot \underline{p}/m} \quad (\text{II-25})$$

where  $\omega_p^2 = 4\pi e^2/m$  is the plasma frequency squared and  $\eta$  is a positive infinitesimal (arising from the assumed asymptotic behavior).

A less restricted approach has recently been given by Guernsey (25), in which the assumptions of spatial homogeneity and implicit time dependence are dropped. In their stead, he considers the initial value problem governed by the ( $S = 1, 2$ ) equations where the deviations from equilibrium of  $F_N^{(1)}$  and  $F_N^{(2)}$  are sufficiently small to allow linearization. The resulting equations provide the basis for studies of how plasmas approach equilibrium as well as non-equilibrium transport processes.\* In spite of linearization, the equations are extremely formidable. Solution of the associated transport problem has not yet been achieved and effectively defines one of the present frontiers of the classical theory.

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\*At low frequencies - the "hydrodynamic" limit - transport properties are obtainable from II-24 for reasons discussed previously

In view of the great difficulties encountered in the second stage of approximation, it appears unlikely that the program will be carried to truncations of the BBGKY hierarchy beyond the second. In a sense, there is not much point in doing so, since if three body correlations significantly alter the equilibrium or transport properties of the system, one expects that four-body effects may also be important and that consequently the whole approach is no longer a viable approximation scheme. This, however, underscores a basic shortcoming of the theory since it is difficult to justify stopping at ( $S = 1, 2$ ) without at least showing that going to the next step introduces negligible corrections. Consequently, until techniques are available for setting bounds on the effects due to the neglected higher correlations, the domains of applicability of the theory will be determined by its agreement with experiment, a situation which though philosophically distasteful is nonetheless not without parallel in theoretical physics.

We have dealt with the classical theory at some length to introduce both the language in which the forthcoming quantum theory will largely be phrased as well as the underlying assumptions and limitations which will be carried over along with the language. We will proceed as if the foregoing discussion were complete, and will thus use this language without further discussion, referring the reader to the cited references and standard texts (e.g. Tolman (26), ter Haar (27)) for more incisive treatments of those points where we have been necessarily cavalier.

### C. Quantum Liouville Equation

We now consider a single isolated quantum mechanical N-particle system whose classical Hamiltonian is given by II-3. The constitution of the system is that given in Section II-A, each particle having an intrinsic spin S. We choose a representation in spin space such that the spin projection of each particle in the +Z direction ( $\sigma_z$ ) is diagonal; i.e. the basis vectors are built up out of single particle spinors  $\xi_\alpha^b$ , so that for the i<sup>th</sup> particle

$$\sigma_z(i) \xi_\alpha^b(i) = \alpha \xi_\alpha^b(i) \quad (\text{II-26})$$

where  $\sigma_z(i)$  is the operator corresponding to a measurement on particle i of  $\sigma_z$  and  $\alpha$  has the possible eigen values -S, ..., +S. The  $\xi_\alpha^b$  are also chosen to be ortho-normal:

$$\xi_\alpha^{b*}(i) \xi_\beta^b(i) = \delta_{\alpha\beta} \quad (\text{II-27})$$

In this representation, the general N-body wave function is written (in configuration space) as

$$\Psi_{(1, \dots, N)}^{(N)} = \sum_{\alpha_1, \dots, \alpha_N = -S}^{+S} \psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\tilde{x}_1, \dots, \tilde{x}_N, t) \xi_{\alpha_1}^{b(1)} \dots \xi_{\alpha_N}^{b(N)} \quad (\text{II-28})$$

where the  $(2S+1)^N$  quantities  $\psi_{\alpha_1, \dots, \alpha_N}^{(N)}$  satisfy the Schroedinger equation

$$\left\{ \sum_{j=1}^N \left[ -\frac{\hbar^2}{2m} \nabla_{\tilde{x}_j}^2 + \frac{g^2}{a} \sum_{\substack{k=1 \\ k \neq j}}^N \phi(\tilde{x}_j - \tilde{x}_k) + g^2 \phi^{\text{ext}}(\tilde{x}_j, t) \right] \right\} \psi_{\alpha_1, \dots, \alpha_N}^{(N)} = i\hbar \frac{\partial}{\partial t} \psi_{\alpha_1, \dots, \alpha_N}^{(N)} \quad (\text{II-29})$$



with the normalization

$$\sum_{\alpha_1, \dots, \alpha_N = -S}^{+S} \int d^3x_1 \dots d^3x_N \psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) = 1 \quad (\text{II-30})$$

Thus, the quantity

$$\psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \quad (\text{II-31})$$

is identified as the joint probability density ( $i=1, \dots, N$ ) of finding particle  $i$  at position  $\underline{x}_i$  with spin projection  $\alpha_i$  at time  $t$ .

Following von Roos (10), we define the quantum-mechanical phase-space distribution function  $*(\text{q.m.d.f.})$ :

$$F_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) \equiv \left(\frac{m}{2\pi\hbar}\right)^{3N} \psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \times \int d^3x'_1 \dots d^3x'_N \left[ \psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \exp\left(\frac{im}{\hbar} \sum_{j=1}^N \underline{v}_j \cdot (\underline{x}'_j - \underline{x}_j)\right) \right] \quad (\text{II-32})$$

which is seen to essentially consist of a product of the configuration and momentum space representations of the wave function  $\psi^{(N)}$ , multiplied by a plane wave. Like the wave function, the q.m.d.f. is complex, unobservable, and merely a calculational aid in the computation of expectation values.

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\*We choose to work in position-velocity space rather than position-momentum space, although retaining the name "phase space". For purposes of comparison, the Wigner (7) q.m.d.f., mentioned in the Introduction, is given by the expression (in the absence of spin):

$$F_{\text{WIGNER}}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) \equiv \left(\frac{m}{2\pi\hbar}\right)^{3N} \int d^3y_1 \dots d^3y_N \left[ \psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}_1 + \frac{1}{2}\underline{y}_1, \dots, \underline{x}_N + \frac{1}{2}\underline{y}_N, t) \times \psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1 - \frac{1}{2}\underline{y}_1, \dots, \underline{x}_N - \frac{1}{2}\underline{y}_N, t) \exp\left(\frac{2im}{\hbar} \sum_{j=1}^N \underline{v}_j \cdot \underline{y}_j\right) \right] \quad (\text{II-32})$$

Before deriving the dynamical equation for  $F^{(N)}$  from II-29, it is instructive to derive some of its basic properties directly from the definition II-32. First, integration of II-32 over the  $3N$  dimensional velocity space  $(\underline{v}_1, \dots, \underline{v}_N)$  gives

$$\int F_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) d^3 \underline{v}_1 \dots d^3 \underline{v}_N = \psi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \times \int d^3 \underline{x}'_1 \dots d^3 \underline{x}'_N \psi_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \prod_{j=1}^N \left[ \left( \frac{m}{2\pi\hbar} \right)^3 \int d^3 \underline{v}_j e^{i \frac{m}{\hbar} \underline{v}_j \cdot (\underline{x}'_j - \underline{x}_j)} \right] \quad (\text{II-33})$$

But

$$\left( \frac{m}{2\pi\hbar} \right)^3 \int d^3 \underline{v}_j e^{i \frac{m}{\hbar} \underline{v}_j \cdot (\underline{x}'_j - \underline{x}_j)} = \delta(\underline{x}'_j - \underline{x}_j) \quad (\text{II-34})$$

where  $\delta(\underline{u})$  is the three-dimensional Dirac delta function. Hence,

$$\int F_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) d^3 \underline{v}_1 \dots d^3 \underline{v}_N = \psi_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \psi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \quad (\text{II-35})$$

Similarly, in terms of the velocity space representation,  $\varphi^{(N)}$ , of  $\psi^{(N)}$ :

$$\varphi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{v}_1, \dots, \underline{v}_N, t) \equiv \left( \frac{m}{2\pi\hbar} \right)^{3N} \int d^3 \underline{x}_1 \dots d^3 \underline{x}_N e^{-i \frac{m}{\hbar} \sum_{j=1}^N \underline{v}_j \cdot \underline{x}_j} \psi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \quad (\text{II-36})$$

one finds

$$\int F_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) d^3 \underline{x}_1 \dots d^3 \underline{x}_N = \varphi_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{v}_1, \dots, \underline{v}_N, t) \varphi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{v}_1, \dots, \underline{v}_N, t) \quad (\text{II-37})$$



Integration of II-35 over configuration space and summation in spin space yields, together with II-30, the normalization condition on  $F^{(N)}$ :

$$\sum_{\alpha_1, \dots, \alpha_N = -5}^{+5} \int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N F_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) = 1 \quad (\text{II-38})$$

Thus, it is seen that  $F^{(N)}$  has the convenient property that integration over half of phase space yields the (quantum-mechanical) probability distribution in the canonically conjugate space. This is a special case of the following more general result.

Let the three Cartesian components of  $\underline{x}_i$  and  $\underline{v}_i$  be denoted by  $x_i^{k_i}$  and  $v_i^{k_i}$  where  $k_i = 1, 2, 3$  and consider the following general real function of the position and velocity of the N-particles:

$$G(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) \equiv \sum_{k_1, \dots, k_N = 1}^3 a_{k_1, \dots, k_N}(\underline{x}_1, \dots, \underline{x}_N, t) \prod_{i=1}^N (v_i^{k_i})^{\beta_i} \quad (\text{II-39})$$

where  $\beta_1, \dots, \beta_N$  are arbitrary non-negative integers. Integration of the product of  $G$  and  $F^{(N)*}$ , the complex conjugate of  $F^{(N)}$ , over all of phase space gives

$$\begin{aligned} \int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N G(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) F_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) = \\ \int d^3x_1 \dots d^3x_N \Psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \left\{ \sum_{k_1, \dots, k_N = 1}^3 a_{k_1, \dots, k_N}(\underline{x}_1, \dots, \underline{x}_N, t) \left( \frac{m}{2\pi\hbar} \right)^{3N} \right. \\ \left. \times \int d^3v_1 \dots d^3v_N d^3x'_1 \dots d^3x'_N \prod_{i=1}^N (v_i^{k_i})^{\beta_i} \exp \left[ -\frac{im}{\hbar} \sum_{j=1}^N \underline{v}_j \cdot (\underline{x}'_j - \underline{x}_j) \right] \Psi_{\alpha_1, \dots, \alpha_N}^{(N)}(\underline{x}'_1, \dots, \underline{x}'_N, t) \right\} \end{aligned} \quad (\text{II-40})$$

The right hand side can then be written in the equivalent form

$$\int d^3x_1 \dots d^3x_N \psi_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \left( \sum_{k_1 \dots k_N=1}^3 a_{k_1 \dots k_N}(\underline{x}_1, \dots, \underline{x}_N, t) \prod_{i=1}^N \left( \frac{\hbar}{im} \frac{\partial}{\partial x_i^{k_i}} \right)^{\beta_i} \right) \\ \times \left( \frac{m}{2\pi\hbar} \right)^{3N} \int d^3v_1 \dots d^3v_N d^3x'_1 \dots d^3x'_N \exp \left[ \frac{im}{\hbar} \sum_{j=1}^N \underline{v}_j \cdot (\underline{x}'_j - \underline{x}_j) \right] \psi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}'_1, \dots, \underline{x}'_N, t) \quad (II-41)$$

Performing the velocity space integration, making use of II-34 and then integrating over the primed configuration space leads to the result\*

$$\int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N G(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) F_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) = \\ \int d^3x_1 \dots d^3x_N \psi_{\alpha_1 \dots \alpha_N}^{(N)*}(\underline{x}_1, \dots, \underline{x}_N, t) \left[ \sum_{k_1 \dots k_N=1}^3 a_{k_1 \dots k_N}(\underline{x}_1, \dots, \underline{x}_N, t) \prod_{i=1}^N \left( \frac{\hbar}{im} \frac{\partial}{\partial x_i^{k_i}} \right)^{\beta_i} \right] \psi_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \quad (II-42)$$

It is therefore seen that the integral over phase space of the product of  $F^{(N)*}$  and a function of the form II-39 is equal to the quantum-mechanical expectation value of the "well-ordered"\*\*\* operator obtained from II-39 by the formal substitution  $\underline{v}_i \rightarrow \frac{\hbar}{im} \nabla_i$ . Now consider the result of integrating the product of  $G$  and  $F^{(N)}$ . In this case, II-42 would be replaced by

$$\int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N G F^{(N)} = \int d^3x_1 \dots d^3x_N \psi_{\alpha_1 \dots \alpha_N}^{(N)} \sum_{k_1 \dots k_N=1}^3 a_{k_1 \dots k_N} \prod_{i=1}^N \left( \frac{\hbar}{im} \frac{\partial}{\partial x_i^{k_i}} \right)^{\beta_i} \psi_{\alpha_1 \dots \alpha_N}^{(N)*} \quad (II-43)$$

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\*Note that equation (14) of Reference 10 is in error on this point.

\*\*\*An operator is said to be well-ordered if it is written in a form where the gradients (i.e. momentum operators) stand to the right of the scalars (i.e. position operators) and hence act first on the wave function. The reverse situation we shall call "anti well-ordered".

Integrating by parts and ignoring the surface terms in the usual fashion (recall that we are using an infinite volume in configuration space), II-43 becomes

$$\int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N G F_{q_1 \dots q_N}^{(N)} = \int d^3x_1 \dots d^3x_N \psi_{q_1 \dots q_N}^{(N)*} \left[ \sum_{k_1 \dots k_N=1}^3 \frac{1}{N!} \left( \frac{\hbar}{im} \frac{\partial}{\partial x_i^{k_i}} \right)^{\beta_i} a_{k_1 \dots k_N} \right] \psi_{q_1 \dots q_N}^{(N)} \quad (\text{II-44})$$

Thus, integration of  $G$  with  $F^{(N)}$  yields the expectation value of the corresponding anti well-ordered operator. Noting that: *i*) the sum of the well-ordered and anti well-ordered operators appearing in II-42 and II-44 is precisely the Hermitean operator which in a quantum-mechanical system "corresponds"\* to the classical function II-39; *ii*) the foregoing derivation can be trivially extended to the case where  $G$  is an infinite sum of terms of the form II-39 (i.e. a Taylor series in velocity space); and *iii*) in view of the symmetric role played by the configuration space and momentum space representations of  $\psi^{(N)}$  in the definition of  $F^{(N)}$ , we could just as well have considered a  $G$  of the form

$$G'(x_1, \dots, x_N; v_1, \dots, v_N; t) \equiv \sum_{k_1 \dots k_N=1}^3 a'_{k_1 \dots k_N}(x_1, \dots, x_N; t) \prod_{i=1}^N (\chi_i^{k_i})^{\beta_i}$$

and used the momentum space representation of  $\psi^{(N)}$ , we are led to the following desired result:

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\*In this regard, viz. the manner by which one constructs Hermitean quantum-mechanical operators which are the analogues of classical functions of coordinates and momenta, formal ambiguities can sometimes arise as pointed out, for example, in Bohm's Quantum Theory, p. 186. Although no physical situations have yet been found which are capable of experimentally distinguishing between alternative Hermitization procedures, this may not always be the case. We therefore emphasize our assumption that the Hermitean quantum operator analogue of II-39 is given by ( $\frac{1}{2}$ ) the sum of the operators occurring in II-42 and II-44.



Let  $G(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t)$  be any real function of the  $N$  single-particle coordinates and velocities which possesses a Taylor series expansion in either (the  $3N$  dimensional) velocity or configuration space and let  $\hat{G}$  be the quantum-mechanical Hermitean operator which corresponds\* to the observable,  $G$ ; then (in Dirac notation):

$$\text{Re} \int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N G F_{q_1 \dots q_N}^{(N)} = \langle \Psi_{q_1 \dots q_N}^{(N)} | \hat{G} | \Psi_{q_1 \dots q_N}^{(N)} \rangle \quad (\text{II-45})$$

where Re denotes "real part".

The foregoing result illustrates a very useful advantage of  $F^{(N)}$  over the wave-function, viz. that not only can operator averages be obtained by the direct integrations with  $F^{(N)}$  of classical C-number quantities, but also that one need never go through the intermediate process of constructing the appropriate quantum-mechanical Hermitean operator (although the caveat contained in the footnote must be borne in mind). We now turn to the derivation of the dynamical equation for  $F^{(N)}$ .

Differentiating the definition II-32 with respect to time and replacing  $\frac{\partial \Psi}{\partial t}$  and  $\frac{\partial \Psi^*}{\partial t}$  by the corresponding left hand sides of the Schroedinger equation II-29 gives

$$\begin{aligned} \frac{\partial F_{q_1 \dots q_N}^{(N)}}{\partial t} = & \frac{-i}{\hbar} \left( \frac{m}{2\pi\hbar} \right)^{3N} \left\{ \left( \sum_{i=1}^N \left[ -\frac{\hbar^2}{2m} \nabla_{\underline{x}_i}^2 + g^2 \sum_{\substack{j=1 \\ j \neq i}}^N \phi(\underline{x}_i - \underline{x}_j) + g^2 \phi^{ext}(\underline{x}_i, t) \right] \Psi_{q_1 \dots q_N}^{(N)} \right) \right. \\ & \times \int d^3x'_1 \dots d^3x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi_{q_1 \dots q_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \\ & - \Psi_{q_1 \dots q_N}^{(N)} \int d^3x'_1 \dots d^3x'_N \\ & \left. \times \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \left\{ \left[ -\frac{\hbar^2}{2m} \nabla_{\underline{x}_i}^2 + g^2 \sum_{\substack{j=1 \\ j \neq i}}^N \phi(\underline{x}'_i - \underline{x}'_j) + g^2 \phi^{ext}(\underline{x}'_i, t) \right] \Psi_{q_1 \dots q_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \right\} \right\} \quad (\text{II-46}) \end{aligned}$$

The first term in II-46 can be rewritten (temporarily dropping the spin

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\*See footnote on page 30.



indices) using the identity

$$\begin{aligned} & (\nabla_{\underline{x}_i}^2 \Psi^{(N)}) \int d^3 x'_1 \dots d^3 x'_N \left[ \exp \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) = \\ & \nabla_{\underline{x}_i}^2 (\Psi^{(N)}) \int d^3 x'_1 \dots d^3 x'_N \left[ \exp \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \\ & - (\Psi^{(N)} \nabla_{\underline{x}_i}^2 + 2 \nabla_{\underline{x}_i} \Psi^{(N)} \cdot \nabla_{\underline{x}_i}) \left( \int d^3 x'_1 \dots d^3 x'_N \left[ \exp \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \right) \end{aligned} \quad (\text{II-47})$$

in the form

$$\begin{aligned} & (\nabla_{\underline{x}_i}^2 \Psi^{(N)}) \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) = \\ & \left( \nabla_{\underline{x}_i}^2 - \frac{m^2}{\hbar^2} \underline{v}_i^2 + \frac{2im}{\hbar} \underline{v}_i \cdot \nabla_{\underline{x}_i} \right) (\Psi^{(N)}) \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \end{aligned} \quad (\text{II-48})$$

Furthermore, two partial integrations in the primed configuration space in the second  $\nabla^2$  term of II-46 lead to

$$\begin{aligned} & \Psi^{(N)} \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \nabla_{\underline{x}'_i}^2 \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) = \\ & - \frac{m^2}{\hbar^2} \underline{v}_i^2 \Psi^{(N)} \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \end{aligned} \quad (\text{II-49})$$

which cancels a similar term in II-48. Thus, II-46 can be rewritten as

$$\begin{aligned} & \frac{\partial F_{\alpha_1, \dots, \alpha_N}^{(N)}}{\partial t} + \sum_{i=1}^N \underline{v}_i \cdot \nabla_{\underline{x}_i} F_{\alpha_1, \dots, \alpha_N}^{(N)} - \frac{i}{2m\hbar} \sum_{i=1}^N \nabla_{\underline{x}_i}^2 F_{\alpha_1, \dots, \alpha_N}^{(N)} = -\frac{i}{\hbar} \left( \frac{m}{2\pi\hbar} \right)^{3N} \left\{ \sum_{i=1}^N g^2 \phi^{\text{ext}}(\underline{x}_i, t) \Psi_{\alpha_1, \dots, \alpha_N}^{(N)} \right. \\ & \times \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \Psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) - \Psi_{\alpha_1, \dots, \alpha_N}^{(N)} \int d^3 x'_1 \dots d^3 x'_N \exp \left[ \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right] \\ & \times \sum_{i=1}^N g^2 \phi^{\text{ext}}(\underline{x}'_i, t) \Psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) + \sum_{i=1}^N \sum_{j \neq i}^N \left[ \frac{g^2}{2} \phi(\underline{x}_i - \underline{x}_j) \Psi_{\alpha_1, \dots, \alpha_N}^{(N)} \int d^3 x'_1 \dots d^3 x'_N \exp \left( \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right) \right. \\ & \times \Psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) - \Psi_{\alpha_1, \dots, \alpha_N}^{(N)} \int d^3 x'_1 \dots d^3 x'_N \exp \left( \frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i) \right) \frac{g^2}{2} \phi(\underline{x}'_i - \underline{x}'_j) \Psi_{\alpha_1, \dots, \alpha_N}^{(N)*}(\underline{x}'_1, \dots, \underline{x}'_N, t) \left. \right\} \end{aligned} \quad (\text{II-50})$$

Consider first the terms containing  $\phi^{\text{ext}}$ . In the second term, expand

$\phi^{\text{ext}}(\underline{x}'_i, t)$  in a Maclaurin series about  $\underline{x}_i$ :

$$\begin{aligned} \phi^{\text{ext}}(\underline{x}'_i, t) &= \phi^{\text{ext}}(\underline{x}_i, t) + \nabla_{\underline{x}_i} \phi^{\text{ext}}(\underline{x}_i, t) \cdot (\underline{x}'_i - \underline{x}_i) + \dots \\ &= \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n \phi^{\text{ext}}(\underline{x}_i, t)}{\partial \underline{x}_i^k \partial \underline{x}_i^L \dots} (\underline{x}'_i - \underline{x}_i)^K (\underline{x}'_i - \underline{x}_i)^L \dots \end{aligned} \quad (\text{II-51})$$

where summation over the Cartesian indices  $K, L, \dots$  is understood, and note that the general term can be rewritten via the relation

$$\begin{aligned} \psi^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) \int d^3x'_1 \dots d^3x'_N \exp\left[\frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i)\right] \left(\frac{q^2}{n!} \frac{\partial^n \phi^{ext}}{\partial x_i^K \partial x_i^L \dots} (\underline{x}'_i - \underline{x}_i)^K (\underline{x}'_i - \underline{x}_i)^L \dots\right) \psi^{(N)*}_{(x'_1, \dots, x'_N, t)} \\ = \frac{q^2}{n!} \left(\frac{\partial^n \phi^{ext}}{\partial x_i^K \partial x_i^L \dots}\right) \left(-\frac{im}{\hbar}\right)^n \frac{\partial^n}{\partial v_i^K \partial v_i^L \dots} \left(\psi^{(N)} \int d^3x'_1 \dots d^3x'_N \exp\left[\frac{im}{\hbar} \sum_{i=1}^N \underline{v}_i \cdot (\underline{x}'_i - \underline{x}_i)\right] \psi^{(N)*}_{(x'_1, \dots, x'_N, t)}\right) \quad (II-52) \end{aligned}$$

If we then define the operator:

$$\begin{aligned} \left[\exp\left[-\frac{i\hbar}{m} \sum_{i=1}^N \nabla_{\underline{x}_i} \cdot \nabla_{\underline{v}_i}\right]\right] (A(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t)) (B(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t)) \\ \equiv AB - \frac{i\hbar}{m} \sum_{i=1}^N \nabla_{\underline{x}_i} \cdot A \cdot \nabla_{\underline{v}_i} B + \frac{1}{2!} \left(-\frac{i\hbar}{m}\right)^2 \sum_{K, L=1}^3 \left(\sum_{i=1}^N \frac{\partial}{\partial x_i^K} \frac{\partial}{\partial v_i^K}\right) \left(\sum_{j=1}^N \frac{\partial}{\partial x_j^L} \frac{\partial}{\partial v_j^L}\right) AB + \dots \quad (II-53) \end{aligned}$$

where the spatial gradients are understood to act on  $A$  alone and the velocity gradients on  $B$  alone, it is easily shown that the first two terms on the r.h.s. of II-50 can be concisely written as

$$-\frac{i}{\hbar} \left[1 - \exp\left[-\frac{i\hbar}{m} \sum_{i=1}^N \nabla_{\underline{x}_i} \cdot \nabla_{\underline{v}_i}\right]\right] \left(q^2 \sum_{j=1}^N \phi^{ext}(\underline{x}_j, t)\right) \left(F^{(N)}_{\alpha, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t)\right) \quad (II-54)$$

Similarly, in the last term of II-50, expand  $\phi(\underline{x}'_i - \underline{x}'_j)$  about the point  $(\underline{x}_i - \underline{x}_j)$ :

$$\begin{aligned} \phi(\underline{x}'_i - \underline{x}'_j) = \phi(\underline{x}_i - \underline{x}_j) + \left[\nabla_{\underline{x}_i} \phi(\underline{x}_i - \underline{x}_j) \cdot (\underline{x}'_i - \underline{x}_i) + \nabla_{\underline{x}_j} \phi(\underline{x}_i - \underline{x}_j) \cdot (\underline{x}'_j - \underline{x}_j)\right] \\ + \frac{1}{2!} \left[\frac{\partial^2 \phi(\underline{x}_i - \underline{x}_j)}{\partial x_i^K \partial x_i^L} (\underline{x}'_i - \underline{x}_i)^K (\underline{x}'_i - \underline{x}_i)^L + \frac{\partial^2 \phi(\underline{x}_i - \underline{x}_j)}{\partial x_i^K \partial x_j^L} (\underline{x}'_i - \underline{x}_i)^K (\underline{x}'_j - \underline{x}_j)^L \right. \\ \left. + \frac{\partial^2 \phi(\underline{x}_i - \underline{x}_j)}{\partial x_j^K \partial x_i^L} (\underline{x}'_j - \underline{x}_j)^K (\underline{x}'_i - \underline{x}_i)^L + \frac{\partial^2 \phi(\underline{x}_i - \underline{x}_j)}{\partial x_j^K \partial x_j^L} (\underline{x}'_j - \underline{x}_j)^K (\underline{x}'_j - \underline{x}_j)^L\right] \quad (II-55) \end{aligned}$$

+ . . .

Then, proceeding analogously to II-52, one finds that the remaining terms on the r.h.s. of II-50 become simply

$$-\frac{i}{\hbar} \left[ 1 - \exp \left[ -\frac{i\hbar}{m} \sum_{i=1}^N \nabla_{\tilde{x}_i} \cdot \nabla_{\tilde{x}_i} \right] \right] \left( \frac{g^2}{2} \sum_{j=1}^N \sum_{\substack{k=1 \\ k \neq j}}^N \phi(\tilde{x}_j - \tilde{x}_k) \right) \left( F_{d_1, \dots, d_N}^{(N)}(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t) \right) \quad \text{II-56}$$

Combining II-50, II-54 and II-56 leads to the desired result, which we can express in an elegant fashion by defining the Generalized Poisson Bracket  $\{A, B\}_{G.P.B.}^{(N)}$  in terms of the operator II-53:

$$\left\{ A(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t), B(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t) \right\}_{G.P.B.}^{(N)} \equiv \frac{i}{\hbar} \left[ \exp \left[ -\frac{i\hbar}{m} \sum_{i=1}^N \nabla_{\tilde{x}_i} \cdot \nabla_{\tilde{x}_i} \right] \right] \left( (A)(B) - (B)(A) \right) \quad \text{II-57}$$

Note that the first term of II-57,

$$\frac{1}{m} \sum_{i=1}^N \left( \nabla_{\tilde{x}_i} A \cdot \nabla_{\tilde{v}_i} B - \nabla_{\tilde{v}_i} A \cdot \nabla_{\tilde{x}_i} B \right) \quad \text{II-58}$$

is just the usual Poisson Bracket; the remaining terms are  $O(\hbar)$  and vanish in the classical limit. In terms of the G.P.B., then, we find after trivial algebra that II-50 becomes simply

$$\frac{\partial F_{d_1, \dots, d_N}^{(N)}}{\partial t} + \left\{ F_{d_1, \dots, d_N}^{(N)}(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t), H_{G.P.B.}^{(N)}(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t) \right\}_{G.P.B.}^{(N)} = 0 \quad \text{II-59}$$

where  $H^{(N)}$  is just the classical Hamiltonian:

$$H^{(N)}(\tilde{x}_1, \dots, \tilde{x}_N; \tilde{v}_1, \dots, \tilde{v}_N; t) \equiv \sum_{i=1}^N \left( \frac{1}{2} m \tilde{v}_i^2 + g^2 \phi^{ext}(\tilde{x}_i; t) + \frac{1}{2} g^2 \sum_{\substack{j=1 \\ j \neq i}}^N \phi(\tilde{x}_i - \tilde{x}_j) \right) \quad \text{II-60}$$



Thus, we are led to the striking result that the Schroedinger equation for an isolated N-body system can be written in a form which closely resembles the classical Liouville equation (c.f. equation II-1) and, in fact, becomes identical to the Liouville equation when  $\hbar \rightarrow 0$ . Recalling that the Liouville equation describes a statistical ensemble of classical systems, whereas II-59 was derived for a single isolated system, it might seem, therefore, that the statistical character of quantum-mechanics persists, in some sense, in the classical limit. This touches on some fundamental issues concerning the interpretation of quantum-mechanics, which continue to be much discussed (23) and which we choose to avoid. One observation, however, is in order. We shall see presently that when the transition to quantum statistical mechanics is made (by introducing a representative ensemble and averaging  $F^{(N)}$  over its members), the ensemble averaged  $F^{(N)}$  satisfies precisely the same equation (II-59) as one obtains for an isolated system. Thus II-59 appears to contain both quantum mechanics and quantum statistical mechanics, depending on how one wishes to interpret  $F^{(N)}$  and what assumptions one makes about its initial or asymptotic time behaviour. Putting it another way: although every solution of the Schroedinger equation II-29 leads to an  $F^{(N)}$  (through the definition II-32) which satisfies II-59, the converse is not true -- II-59 admits solutions which cannot be interpreted as characterizing a single isolated system.

To illustrate this point, consider an isolated system in an energy eigenstate,  $E_a$ , with eigenfunction  $\Psi_a^{(N)}$ . Since the time dependence of  $\Psi_a^{(N)}$  is contained solely in a factor  $e^{-iE_a t/\hbar}$ , one sees from the definition II-32 that the consequent  $F_a^{(N)}$  is time independent and consequently satis-



fies the equation

$$\left\{ F_a^{(N)}, H^{(N)} \right\}_{G.P.B.}^{(N)} = 0 \quad (\text{II-61})$$

Since II-61 is linear in  $F^{(N)}$ , it will also be satisfied by  $\frac{1}{2} (F_a^{(N)} + F_b^{(N)})$ , where  $b$  corresponds to a different energy eigenstate. This quantity, however, arises from a wave function

$$\frac{1}{\sqrt{2}} \left( e^{i\phi_a} \Psi_a^{(N)} + e^{i\phi_b} \Psi_b^{(N)} \right) \quad (\text{II-62})$$

where the phases  $\phi_a$  and  $\phi_b$  are random and thus characterizes not a single system but rather a (stationary) statistical ensemble of systems.

Now in this dissertation we shall be concerned with two general categories of problems: *i*) a description of the energy eigenstates of isolated systems (the so-called "pure case"), and *ii*) the statistical mechanics of systems in contact with a thermostat ("mixed case"). The second type of problem will be handled naturally by the introduction of representative macrocanonical ensembles along lines parallel to the development sketched in section II-B. To treat the first category, however, we need a prescription for distinguishing those solutions of II-61 which properly represent an isolated system from those appropriate to a stationary ensemble since, as we have noted, both situations are contained in this equation. The requisite condition is obtained simply from the relation II-45 by requiring that the energy calculated from  $F^{(N)}$  should be "sharp", i.e. if

$$\overline{E} \equiv R_0 \int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N H^{(N)} F^{(N)} \quad (\text{II-63})$$

then

$$\overline{(\Delta E)^2} \equiv \mathcal{R}_0 \int d^3x_1 \dots d^3x_N d^3v_1 \dots d^3v_N (H^{(N)} - \bar{E})^2 F^{(N)} = 0 \quad (\text{II-64})$$

for a "pure state". It is readily verified that II-64 will not hold, for example, in the case  $F^{(N)} = \frac{1}{2} (F_a^{(N)} + F_b^{(N)})$  considered previously. In many cases, particularly those where we wish to study the ground state of an isolated system, it will not be necessary to make explicit use of II-64 since we can simply pass to the limit of zero temperature in the corresponding statistical quantum mechanical problem. Alternatively, since an isolated system in an energy eigenstate is equivalent to a microcanonical ensemble, we can without loss of generality deal exclusively with ensemble averaged q.m.d.f.'s in the forthcoming formalism, choosing a microcanonical ensemble in the pure case and the macrocanonical ensemble in the mixed case. At zero temperature, the macrocanonical ensemble becomes identical to a microcanonical ensemble of systems in the ground state.

The transition to quantum statistical mechanics can now be easily made as follows: Recall that a single system is in general described by the  $(2S+1)^N$  quantities  $F_{\alpha_1 \dots \alpha_N}^{(N)}$ , each of which satisfies II-59. Representing the totality of such quantities symbolically as  $F_{\alpha}^{(N)}$ , consider an ensemble of N-body systems, the  $i^{\text{th}}$  member of which is characterized by  $F_{\alpha}^{(N)}(i)$  and a normalized statistical weight  $w_i$ . The quantum mechanical ensemble distribution function,  $\widetilde{F}_{\alpha}^{(N)}$  is then defined simply as\*

$$\widetilde{F}_{\alpha}^{(N)} \equiv \sum_i w_i F_{\alpha}^{(N)}(i) \quad (\text{II-65})$$

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\*Note that in the usual formulation of quantum statistical mechanics, one averages the wave function over an ensemble whereas we average the q.m.d.f. which is bilinear in the wave function. It is readily shown that the two approaches are equivalent if the wave functions are averaged with random phases so that interferences between different members of the ensemble vanish, an assumption which is always made.

Since II-59 is linear in  $F_\alpha^{(N)}$  and the  $W_i$  are just numbers, we see that  $F_\alpha^{(N)}$  and  $\widetilde{F}_\alpha^{(N)}$  satisfy precisely the same equation as mentioned earlier.

Equation II-59, therefore, when written in terms of  $\widetilde{F}_\alpha^{(N)}$ , represents the starting point of our quantum many-body theory, which will proceed from this equation in more or less strict analogy to the development of the classical theory from the Liouville equation, as sketched in section II-B. The first step of this development is the introduction of "reduced" q.m.d.f.'s and the derivation of the quantum analogue of the B.B.G.K.Y Hierarchy.

Before proceeding, however, one final question must be discussed, viz. the symmetry properties of the  $F_\alpha^{(N)}$ . The necessity for this arises from the fact that the Schrödinger equation II-29 does not in itself completely determine the wave function II-23. To it must be adjoined the symmetry property

$$\Psi^{(N)}(i_1, \dots, i_l, \dots, j, \dots, N) = \pm \Psi^{(N)}(i_1, \dots, j, \dots, i_l, \dots, N) \quad (\text{II-66})$$

where the + sign obtains if S is integral, - if half integral. This condition will likewise impose certain restrictions on the  $F_\alpha^{(N)}$  (and consequently the  $\widetilde{F}_\alpha^{(N)}$ ) which we now investigate.

In terms of the  $\Psi_{\alpha_1, \dots, \alpha_N}^{(N)}$  (see II-28), II-66 can be written

$$\Psi_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N, t) = \pm \Psi_{\alpha_1, \dots, \alpha_j, \dots, \alpha_i, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N, t) \quad (\text{II-67})$$

Using this equation and the definition II-32, we find that interchange of the spatial coordinates of particles  $i$  and  $j$  leads to

$$\begin{aligned} F_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) &= \left(\frac{m}{2\pi\hbar}\right)^{3N} (\pm) \Psi_{\alpha_1, \dots, \alpha_j, \dots, \alpha_i, \dots, \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N, t) \\ &\times \exp\left[-\frac{im}{\hbar}(\underline{v}_i \cdot \underline{x}_i + \dots \underline{v}_i \cdot \underline{x}_j + \dots \underline{v}_j \cdot \underline{x}_i + \dots \underline{v}_j \cdot \underline{x}_N)\right] \int d^3x'_1 \dots d^3x'_N \exp\left[\frac{im}{\hbar}(\underline{v}_i \cdot \underline{x}'_i + \dots \underline{v}_i \cdot \underline{x}'_j + \dots \underline{v}_j \cdot \underline{x}'_i + \dots \underline{v}_j \cdot \underline{x}'_N)\right] \\ &\times \Psi_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}^{(N)}(\underline{x}'_1, \dots, \underline{x}'_j, \dots, \underline{x}'_i, \dots, \underline{x}'_N, t) \end{aligned} \quad (\text{II-68})$$



Interchange of the dummy variables  $\chi'_i$  and  $\chi'_j$  leads to the desired relation

$$F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) = F^{(N)}_{\alpha_1, \dots, \alpha_j, \dots, \alpha_i, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_j, \dots, \underline{v}_i, \dots, \underline{v}_N; t) \quad (\text{II-69})$$

In the special case where  $\alpha_i = \alpha_j$ , however, a stronger condition can be derived

$$F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) = \pm e^{\frac{im}{\hbar}(\underline{v}_i - \underline{v}_j) \cdot (\underline{x}_i - \underline{x}_j)} \times F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) \quad \text{if } \alpha_i = \alpha_j \quad (\text{II-70})$$

Similarly, interchange of the velocity coordinates of particles  $i$  and  $j$  yields in general

$$F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_j, \dots, \underline{v}_i, \dots, \underline{v}_N; t) = F^{(N)}_{\alpha_1, \dots, \alpha_j, \dots, \alpha_i, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) \quad (\text{II-71})$$

and in the special case  $\alpha_i = \alpha_j$  gives the stronger requirement

$$F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_j, \dots, \underline{v}_i, \dots, \underline{v}_N; t) = \pm e^{\frac{im}{\hbar}(\underline{v}_i - \underline{v}_j) \cdot (\underline{x}_i - \underline{x}_j)} \times F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) \quad \text{if } \alpha_i = \alpha_j \quad (\text{II-72})$$

Finally, interchange of the spin indices  $\alpha_i$  and  $\alpha_j$  gives

$$F^{(N)}_{\alpha_1, \dots, \alpha_j, \dots, \alpha_i, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_i, \dots, \underline{x}_j, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_i, \dots, \underline{v}_j, \dots, \underline{v}_N; t) = F^{(N)}_{\alpha_1, \dots, \alpha_i, \dots, \alpha_j, \dots, \alpha_N}(\underline{x}_1, \dots, \underline{x}_j, \dots, \underline{x}_i, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_j, \dots, \underline{v}_i, \dots, \underline{v}_N; t) \quad (\text{II-73})$$

Thus it is seen that in general, spin, position and velocity play identical roles in the symmetry properties of  $F_q^{(N)}$ : an interchange among one is equal to the simultaneous interchange among the other two. In the special case of equal spin indices, the more powerful conditions II-70 and II-72 apply.



#### D. Quantum BBGKY Hierarchy

The basic equations of the theory are II-59 (written in terms of  $\widetilde{F}_\alpha^{(N)}$ ) and the symmetry conditions II-69 - II-73. We propose to attack them by deriving the quantum analog of the B.B.G.K.Y hierarchy II-11. To this end, define the reduced q.m.d.f.'s

$$\widetilde{F}_{\alpha_1 \dots \alpha_R}^{(R)}(\underline{x}_1, \dots, \underline{x}_R; \underline{v}_1, \dots, \underline{v}_R; t) \equiv \sum_{\alpha_{R+1} \dots \alpha_N = -S}^{+S} \int d^3x_{R+1} \dots d^3x_N d^3v_{R+1} \dots d^3v_N \widetilde{F}_{\alpha_1 \dots \alpha_N}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) \quad (\text{II-74})$$

Integrating II-59 over the subspace  $(\underline{x}_{R+1} \dots \underline{x}_N; \underline{v}_{R+1} \dots \underline{v}_N)$  and summing over the spin indices  $\alpha_{R+1} \dots \alpha_N$  yields the equation

$$\begin{aligned} \frac{\partial \widetilde{F}_{\alpha_1 \dots \alpha_R}^{(R)}}{\partial t} + \left\{ \widetilde{F}_{\alpha_1 \dots \alpha_R}^{(R)}(\underline{x}_1, \dots, \underline{x}_R; \underline{v}_1, \dots, \underline{v}_R; t), H^{(R)}(\underline{x}_1, \dots, \underline{x}_R; \underline{v}_1, \dots, \underline{v}_R; t) \right\}_{\text{G.P.B.}}^{(R)} \\ = \sum_{\alpha_{R+1} \dots \alpha_N = -S}^{+S} \int d^3x_{R+1} \dots d^3x_N d^3v_{R+1} \dots d^3v_N \sum_{j=1}^R \sum_{k=R+1}^N \frac{i}{\hbar} \left[ \exp \left[ \frac{-i\hbar}{m} \nabla_{\underline{x}_j} \cdot \nabla_{\underline{v}_j} \right] - 1 \right] (g^2 \phi(\underline{x}_j - \underline{x}_k)) \left( \widetilde{F}_{\alpha_1 \dots \alpha_N}^{(N)} \right) \quad (\text{II-75}) \end{aligned}$$

where surface terms have been dropped as usual in the requisite partial integrations in position and velocity space. Using the symmetry condition II-73 (which holds as well for  $\widetilde{F}_\alpha^{(N)}$ ), the sum over  $k$  can be collapsed in II-75 to yield the desired analog of II-11:

$$\begin{aligned} \frac{\partial \widetilde{F}_{\alpha_1 \dots \alpha_R}^{(R)}}{\partial t} + \left\{ \widetilde{F}_{\alpha_1 \dots \alpha_R}^{(R)}(\underline{x}_1, \dots, \underline{x}_R; \underline{v}_1, \dots, \underline{v}_R; t), H^{(R)}(\underline{x}_1, \dots, \underline{x}_R; \underline{v}_1, \dots, \underline{v}_R; t) \right\}_{\text{G.P.B.}}^{(R)} \\ = (N-R)g^2 \sum_{j=1}^R \sum_{\alpha_{R+1} = -S}^{+S} \int d^3x_{R+1} d^3v_{R+1} \frac{i}{\hbar} \left[ \exp \left[ \frac{-i\hbar}{m} \nabla_{\underline{x}_j} \cdot \nabla_{\underline{v}_j} \right] - 1 \right] (\phi(\underline{x}_j - \underline{x}_{R+1})) \left( \widetilde{F}_{\alpha_1 \dots \alpha_{R+1}}^{(R+1)} \right) \quad (\text{II-76}) \end{aligned}$$

To this equation must naturally be added the appropriate symmetry properties which are derived straightforwardly from II-69 - II-73. The results are simply represented by replacing  $N$  by  $R$  in these equations so we will not repeat them here.

Of particular interest are the R=1,2 equations of II-76. Writing out

the generalized Poisson Brackets explicitly, we find for R=1:

$$\begin{aligned} \frac{\partial \tilde{F}_{\alpha_1}^{(1)}}{\partial t} + \tilde{v}_1 \cdot \nabla_{\tilde{x}_1} \tilde{F}_{\alpha_1}^{(1)} - \frac{i\hbar}{2m} \nabla_{\tilde{x}_1}^2 \tilde{F}_{\alpha_1}^{(1)} - \frac{i g^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n \phi^{\text{ext}}(\tilde{x}_1, t)}{\partial x_1^{\kappa} \partial x_1^{\lambda} \dots} \frac{\partial^n \tilde{F}_{\alpha_1}^{(1)}(\tilde{x}_1, \tilde{v}_1, t)}{\partial v_1^{\kappa} \partial v_1^{\lambda} \dots} \\ = (N-1) g^2 \sum_{\alpha_2=-S}^{+S} \int d^3 \tilde{x}_2 d^3 \tilde{v}_2 \sum_{n=1}^{\infty} \frac{i}{\hbar} \left( \frac{-i\hbar}{m} \right)^n \frac{1}{n!} \frac{\partial^n \phi(\tilde{x}_1 - \tilde{x}_2)}{\partial x_1^{\kappa} \partial x_1^{\lambda} \dots} \frac{\partial^n \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{v}_1, \tilde{v}_2; t)}{\partial v_1^{\kappa} \partial v_1^{\lambda} \dots} \quad (\text{II-77}) \end{aligned}$$

where summation over the Cartesian indices  $\kappa, \lambda, \dots$  is implied. We will find it convenient in some applications to rewrite this equation in a somewhat different but equivalent form. To this end, we introduce the Fourier transforms of the interaction and external potentials:

$$\begin{aligned} \phi(\tilde{x}_1 - \tilde{x}_2) &\equiv \frac{1}{(2\pi)^3} \int d^3 q e^{i q \cdot (\tilde{x}_1 - \tilde{x}_2)} f(q) \\ \phi^{\text{ext}}(\tilde{x}_1, t) &\equiv \frac{1}{(2\pi)^3} \int d^3 q e^{i q \cdot \tilde{x}_1} f^{\text{ext}}(q, t) \quad (\text{II-78}) \end{aligned}$$

In terms of these transforms, it is easily shown that II-77 becomes

$$\begin{aligned} \frac{\partial \tilde{F}_{\alpha_1}^{(1)}}{\partial t} + \tilde{v}_1 \cdot \nabla_{\tilde{x}_1} \tilde{F}_{\alpha_1}^{(1)} - \frac{i\hbar}{2m} \nabla_{\tilde{x}_1}^2 \tilde{F}_{\alpha_1}^{(1)} - \frac{i g^2}{\hbar} \int d^3 q e^{i q \cdot \tilde{x}_1} f^{\text{ext}}(q, t) \left[ \tilde{F}_{\alpha_1}^{(1)}(\tilde{x}_1, \tilde{v}_1 + \frac{\hbar}{m} q, t) - \tilde{F}_{\alpha_1}^{(1)}(\tilde{x}_1, \tilde{v}_1, t) \right] \\ = \frac{i}{\hbar} (N-1) g^2 \sum_{\alpha_2=-S}^{+S} \int d^3 \tilde{x}_2 d^3 \tilde{v}_2 d^3 q e^{i q \cdot (\tilde{x}_1 - \tilde{x}_2)} f(q) \left[ \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{v}_1 + \frac{\hbar}{m} q, \tilde{v}_2, t) - \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{v}_1, \tilde{v}_2, t) \right] \quad (\text{II-79}) \end{aligned}$$

In a similar fashion, we find for the R=2 equation the two equivalent forms:

$$\begin{aligned} \left[ \frac{\partial}{\partial t} + \tilde{v}_1 \cdot \nabla_{\tilde{x}_1} + \tilde{v}_2 \cdot \nabla_{\tilde{x}_2} - \frac{i\hbar}{2m} \nabla_{\tilde{x}_1}^2 - \frac{i\hbar}{2m} \nabla_{\tilde{x}_2}^2 - \frac{i g^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n \phi^{\text{ext}}(\tilde{x}_1, t)}{\partial x_1^{\kappa} \partial x_1^{\lambda} \dots} \frac{\partial^n}{\partial v_1^{\kappa} \partial v_1^{\lambda} \dots} \right. \\ \left. - \frac{i g^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n \phi^{\text{ext}}(\tilde{x}_2, t)}{\partial x_2^{\kappa} \partial x_2^{\lambda} \dots} \frac{\partial^n}{\partial v_2^{\kappa} \partial v_2^{\lambda} \dots} \right] \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{v}_1, \tilde{v}_2; t) = \\ \frac{i g^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \left[ \left( \frac{\partial}{\partial x_1^{\kappa}} \frac{\partial}{\partial v_1^{\kappa}} + \frac{\partial}{\partial x_2^{\kappa}} \frac{\partial}{\partial v_2^{\kappa}} \right) \left( \frac{\partial}{\partial x_1^{\lambda}} \frac{\partial}{\partial v_1^{\lambda}} + \frac{\partial}{\partial x_2^{\lambda}} \frac{\partial}{\partial v_2^{\lambda}} \right) \dots \right] (\phi(\tilde{x}_1 - \tilde{x}_2)) \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\tilde{x}_1, \tilde{x}_2; \tilde{v}_1, \tilde{v}_2; t) \\ + (N-2) \frac{i g^2}{\hbar} \sum_{\alpha_3=-S}^S \int d^3 \tilde{x}_3 d^3 \tilde{v}_3 \sum_{n=1}^{\infty} \left( \frac{-i\hbar}{m} \right)^n \frac{1}{n!} \frac{\partial^n \phi(\tilde{x}_1 - \tilde{x}_3)}{\partial x_1^{\kappa} \partial x_1^{\lambda} \dots} \frac{\partial^n \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\tilde{x}_1, \tilde{x}_2, \tilde{x}_3; \tilde{v}_1, \tilde{v}_2, \tilde{v}_3; t)}{\partial v_1^{\kappa} \partial v_1^{\lambda} \dots} \\ + (N-2) \frac{i g^2}{\hbar} \sum_{\alpha_3=-S}^S \int d^3 \tilde{x}_3 d^3 \tilde{v}_3 \sum_{n=1}^{\infty} \left( \frac{-i\hbar}{m} \right)^n \frac{1}{n!} \frac{\partial^n \phi(\tilde{x}_2 - \tilde{x}_3)}{\partial x_2^{\kappa} \partial x_2^{\lambda} \dots} \frac{\partial^n \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\tilde{x}_1, \tilde{x}_2, \tilde{x}_3; \tilde{v}_1, \tilde{v}_2, \tilde{v}_3; t)}{\partial v_2^{\kappa} \partial v_2^{\lambda} \dots} \quad (\text{II-80}) \end{aligned}$$

$$\begin{aligned}
 & \text{and } \left[ \frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_{\vec{x}_1} + \vec{v}_2 \cdot \nabla_{\vec{x}_2} - \frac{i\hbar}{2m} \nabla_{\vec{x}_1}^2 - \frac{i\hbar}{2m} \nabla_{\vec{x}_2}^2 \right] \widetilde{F}_{\alpha, \alpha_2}^{(2)} - \left[ \frac{ig^2}{\hbar (2\pi)^3} \int d^3 q e^{i\vec{q} \cdot \vec{x}} \right. \\
 & \times f^{ext}(\vec{q}, t) \left( \widetilde{F}_{\alpha, \alpha_2}^{(2)}(\vec{x}_1, \vec{x}_2; \vec{v}_1 + \frac{\hbar}{m} \vec{q}, \vec{v}_2; t) - \widetilde{F}_{\alpha, \alpha_2}^{(2)}(\vec{x}_1, \vec{x}_2; \vec{v}_1, \vec{v}_2; t) \right) + \{1 \leftrightarrow 2\} \Big] \\
 & = \frac{ig^2}{\hbar (2\pi)^3} \int d^3 q e^{i\vec{q} \cdot (\vec{x}_1 - \vec{x}_2)} f(\vec{q}) \left( \widetilde{F}_{\alpha, \alpha_2}^{(2)}(\vec{x}_1, \vec{x}_2; \vec{v}_1 + \frac{\hbar}{m} \vec{q}, \vec{v}_2 - \frac{\hbar}{m} \vec{q}; t) - \widetilde{F}_{\alpha, \alpha_2}^{(2)}(\vec{x}_1, \vec{x}_2; \vec{v}_1, \vec{v}_2; t) \right) \\
 & + \left[ \frac{i(N-2)g^2}{\hbar (2\pi)^3} \sum_{\alpha_3=-S}^S \int d^3 x_3 d^3 v_3 d^3 q e^{i\vec{q} \cdot (\vec{x}_1 - \vec{x}_3)} f(\vec{q}) \left( \widetilde{F}_{\alpha, \alpha_2 \alpha_3}^{(3)}(\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{v}_1 + \frac{\hbar}{m} \vec{q}, \vec{v}_2, \vec{v}_3; t) - \widetilde{F}_{\alpha, \alpha_2 \alpha_3}^{(3)}(\vec{x}_1, \vec{x}_2, \vec{x}_3; \vec{v}_1, \vec{v}_2, \vec{v}_3; t) \right) \right. \\
 & \left. + \{1 \leftrightarrow 2\} \right] \quad (II-81)
 \end{aligned}$$

These equations, then, together with the associated symmetry conditions (obtained by setting  $N=1,2,3$  in II-69 - II-73) represent the quantum analogues of the first two members of the classical B.B.G.K.Y. hierarchy. Aside from the more complicated operators involved (i.e. the difference between Generalized and ordinary Poisson Brackets), they differ from the classical equations in two significant respects. The first arises from the presence of the spin indices. Whereas in the classical case, only a single  $F^{(1)}, F^{(2)}, \dots$  is required, here we have in general  $(2S+1) \widetilde{F}^{(1)}_S, (2S+1)^2 \widetilde{F}^{(2)}_S$ , and so forth.\* The second difference is the presence of the auxiliary symmetry conditions which, being far more stringent than the classical relation II-7, severely restrict the possible forms of the q.m.d.f. Thus, while we might be tempted to try an approximation scheme based on successive ansatzes of the form II-13 and II-14, we would find ourselves in violation of the symmetry conditions II-70 and II-72 at each stage of approximation. This will be shown to be tantamount to the neglect of exchange effects, and

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\*The  $(2S+1)^R \widetilde{F}^{(R)}_S$  are, of course, not independent, being related by the symmetry conditions as well as the constraints on the total spin of the system ( $\sum \vec{S}_i$ ) and its  $z$  projection ( $\sum S_{iz}$ ) which commute with the Hamiltonian and hence can be considered as prescribed for each member of the ensemble. Examples of such constraints are:

$$\begin{aligned}
 & \sum_{\alpha_i=-S}^S \alpha_i \int d^3 x_i d^3 v_i \widetilde{F}_{\alpha_i}^{(1)}(\vec{x}_i, \vec{v}_i, t) = \sum_z z / N \\
 & \text{and} \quad \widetilde{F}_{\alpha_1 \dots \alpha_N}^{(N)} = 0 \quad \text{if } \alpha_1 + \dots + \alpha_N \neq \sum_z z
 \end{aligned}$$

leads to a description of systems of particles obeying Maxwell-Boltzmann statistics. While this may not be a serious limitation in some situations, a more involved scheme of successive approximations is clearly required in the general case.

The procedure we shall adopt is as follows. The first stage of approximation is to close (the  $R=1$ ) equation II-79 with the ansatz

$$\widetilde{F}_{\alpha_1 \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2, t) = \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \quad (\text{II-82})$$

which, while in conformity with the symmetry conditions II-69, II-71 and II-73, is nevertheless in conflict with II-70 and II-72 when  $\alpha_1 = \alpha_2$ . II-82 is the direct analogue of II-13 and corresponds to the neglect of all two-body correlations. For reasons to be discussed presently, we call this the statistical Hartree approximation.

At the second stage, we still deal only with II-79, but choose a decomposition of  $\widetilde{F}^{(2)}$  in terms of  $\widetilde{F}^{(1)}$ 's which explicitly satisfies the full set of symmetry conditions. It is readily verified that this can be achieved by the ansatz

$$\widetilde{F}_{\alpha_1 \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2, t) = \begin{cases} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) & \text{if } \alpha_1 \neq \alpha_2 \\ C \left[ \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \pm e^{\frac{-im}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right. \\ \quad \left. \times \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_1, t) \right] & \text{if } \alpha_1 = \alpha_2 \end{cases} \quad (\text{II-83})$$

where  $C$  is a normalizing constant and the  $+$  sign obtains if  $S$  is integral, - if  $S$  is half-integral. As an aside, we also exhibit the appropriate decomposition of  $\widetilde{F}^{(3)}$  in terms of  $\widetilde{F}^{(1)}$ 's which, while not needed at this



point, will guide us in going to the third stage of approximation:

$$\begin{aligned}
 & \widetilde{F}_{\alpha, \alpha_2, \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3; t) = \\
 & \quad C \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_3, t) \quad \text{if } \alpha_1 \neq \alpha_2 \neq \alpha_3 \\
 & \quad - - - - - \\
 & \quad C' \left[ \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \pm e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_1, t) \right] \\
 & \quad \times \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_3, t) \quad \text{if } \alpha_1 = \alpha_2 \neq \alpha_3 \\
 & \quad - - - - - \\
 & \quad (\text{analogous terms if } \alpha_1 = \alpha_3 \neq \alpha_2 \quad \text{and} \quad \alpha_2 = \alpha_3 \neq \alpha_1) \\
 & \quad - - - - - \\
 & \quad C'' \left[ \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_3, t) \right. \\
 & \quad \pm e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_2) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_1) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_3) \\
 & \quad \pm e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_3) \cdot (\underline{x}_1 - \underline{x}_3)} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_3) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_1) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2) \\
 & \quad \pm e^{-\frac{i m}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_3) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_2) \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1) \\
 & \quad + e^{-\frac{i m}{\hbar}(\underline{v}_2 - \underline{v}_1) \cdot \underline{x}_2} e^{-\frac{i m}{\hbar}(\underline{v}_3 - \underline{v}_2) \cdot \underline{x}_3} e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_3) \cdot \underline{x}_1} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_3) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_1) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_2) \\
 & \quad \left. + e^{-\frac{i m}{\hbar}(\underline{v}_3 - \underline{v}_1) \cdot \underline{x}_3} e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot \underline{x}_1} e^{-\frac{i m}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot \underline{x}_2} \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_2) \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_3) \widetilde{F}_{\alpha_3}^{(1)}(\underline{x}_3, \underline{v}_1) \right] \\
 & \quad \text{if } \alpha_1 = \alpha_2 = \alpha_3
 \end{aligned}$$

(II-84)

Since the second stage II-83 (or the "Hartree-Fock" approximation as we shall call it) still is confined to a consideration of only the  $R=1$  equation, dynamical two-body correlations (i.e. "collisions") are consequently ignored and, as in the classical case, one must ultimately appeal to an explicit choice of the representative ensemble or to a quantum-mechanical H-theorem to remedy this neglect. Nevertheless, again as in the classical case, this approximation (as well as the "Hartree" approximation) has

considerable physical content and utility. In the next two chapters, we will explore these approximations in some detail and, in the process, will establish contact with conventional approximation schemes based on assumptions as to the form of the  $N$ -particle wave function. The reasons for the nomenclature "statistical Hartree" and "Hartree-Fock" as well as the form of II-83 and II-84 will then be made clear.

Proceeding further, in the third stage of approximation we introduce two-body correlations explicitly by working with both the  $R=1$  and  $R=2$  equations, closed by an ansatz expressing  $\tilde{F}^{(3)}$  in terms of  $\tilde{F}^{(1)}$ 's and  $\tilde{F}^{(2)}$ 's. As should now be apparent, we do not at this point force  $\tilde{F}^{(3)}$  to explicitly embody the full symmetry conditions. This is left to the fourth stage of approximation where we still deal only with the  $R=1$  and  $R=2$  equations, but with the proper symmetry, in the fashion of II-83 vis-a-vis II-82. Specifically, the third approximation is defined by taking

$$\begin{aligned} \tilde{F}_{\alpha, \alpha_2 \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3; t) = & \left( \tilde{F}_{\alpha, \alpha_2 \alpha_3}^{(3)} \right)_{\text{eq. II-84}} + \tilde{F}_{\alpha, \underline{x}_1, \underline{v}_1, t}^{(1)} \tilde{G}_{\alpha_2 \alpha_3}^{(2)}(\underline{x}_2, \underline{x}_3; \underline{v}_2, \underline{v}_3; t) \\ & + \tilde{F}_{\alpha_2 \underline{x}_2, \underline{v}_2, t}^{(1)} \tilde{G}_{\alpha, \alpha_3}^{(2)}(\underline{x}_1, \underline{x}_3; \underline{v}_1, \underline{v}_3; t) + \tilde{F}_{\alpha_3 \underline{x}_3, \underline{v}_3, t}^{(1)} \tilde{G}_{\alpha, \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2; t) \end{aligned} \quad (\text{II-85})$$

where the correlation functions,  $\tilde{G}^{(2)}$ , represent the improvement of this approximation over "Hartree-Fock". At the fourth stage, II-85 is amended by explicit symmetrization of the  $\tilde{F}^{(1)} \tilde{G}^{(2)}$  terms in the manner of II-84.

Thus, it is seen that in principle the quantum B.B.G.K.Y. hierarchy is attacked by including correlations between a successively greater number of particles, but in twice as many distinct steps as compared to the

classical case. In general, the  $(2R-1)$ th approximation represents the first introduction of R-body correlations, but without concern about the proper explicit symmetrization of  $\tilde{F}^{(R+1)}$  -- a symmetrization which takes place in the  $2R^{\text{th}}$  approximation.

We will return to the third stage of approximation in Chapters VI and VII where a specific example, the uniform electron gas, is treated in some detail and should clarify the foregoing ideas. We should state in advance, however, what one expects to accomplish in general by going beyond the "Hartree-Fock" approximation. The answer is clear from a consideration of the classical situation outlined in II-B. First, a quantum-mechanical generalization of the "collision integral" II-24 is obtained which serves both to determine the equilibrium value of  $\tilde{F}^{(1)}$  (thereby obviating the necessity for an outside appeal to the H-theorem or ensemble theory) as well as the non-equilibrium and transport properties of the system. Furthermore, the consequent corrections to  $\tilde{F}^{(2)}$  will lead to a more accurate expression for the internal energy of the system and other thermodynamic quantities.

Chapter III.

The Statistical Hartree Approximation

A. General Remarks

Before investigating the consequences of the ansatz II-82, we wish to explore its connection with the so-called Hartree(29) or "self consistent field" approximation in quantum mechanics. For simplicity, we shall assume we are dealing with a spinless system.

The Hartree approximation is characterized by the assumption that the N-body wave function,  $\Psi^{(N)}$ , can be adequately represented as the direct product of N single particle wave functions:

$$\Psi^{(N)}(\underline{x}_1, \dots, \underline{x}_N, t) = \Psi_1(\underline{x}_1, t) \Psi_2(\underline{x}_2, t) \dots \Psi_N(\underline{x}_N, t) \quad (\text{III-1})$$

where the  $\Psi_i$  are in general different and normalized to unity. Although in manifest violation of the requisite symmetry condition II-66, this approximation, by virtue of its inherent simplicity, represents the usual starting point in studies of quantum mechanical many-body systems. When inserted into the Schroedinger equation II-29, III-1 yields a set of N coupled equations for the  $\Psi_i$ , each of which has the form of a single particle Schroedinger equation whose interaction term is the sum of the external field (if any) and the potential arising from the charge density of the other particles.

Consider the "pure case" of an isolated system described by a wave function of the form III-1. It follows directly from the definitions II-28 and II-32 that the consequent N-particle q.m.d.f. is

$$F^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) = \prod_{i=1}^N F_{(i)}(\underline{x}_i, \underline{v}_i, t) \quad (\text{III-2})$$



where

$$F_{(i)}(\underline{x}, \underline{v}, t) \equiv \left(\frac{m}{2\pi\hbar}\right)^3 \psi_i(\underline{x}, t) \int d^3x' \psi_i^*(\underline{x}', t) e^{i\frac{m}{\hbar} \underline{v} \cdot (\underline{x}' - \underline{x})} \quad (\text{III-3})$$

Now since the observable properties of the system do not depend on the labelling of the particles, we can without loss of generality consider an ensemble of  $N!$  systems, each of which has a product decomposition of the form III-2, but which differ in the way the particles are numbered. Specifically, let

$$\widetilde{F}^{(N)}(\underline{x}_1, \dots, \underline{x}_N; \underline{v}_1, \dots, \underline{v}_N; t) \equiv \frac{1}{N!} \sum_{P(j)} \prod_{i=1}^N F_j(\underline{x}_i, \underline{v}_i, t) \quad (\text{III-4})$$

where the summation is over the  $N!$  permutations of 1, 2, ...,  $N$ . Integrating III-4 over  $(\underline{x}_2, \dots, \underline{x}_N; \underline{v}_2, \dots, \underline{v}_N)$ , we find

$$\widetilde{F}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2; t) = \frac{1}{N(N-1)} \sum_{i=1}^N \sum_{\substack{j=1 \\ j \neq i}}^N F_i(\underline{x}_1, \underline{v}_1, t) F_j(\underline{x}_2, \underline{v}_2, t) \quad (\text{III-5})$$

Integration of (III-5) over  $(\underline{x}_2, \underline{v}_2)$  gives

$$\widetilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t) = \frac{1}{N} \sum_{i=1}^N F_i(\underline{x}_1, \underline{v}_1, t) \quad (\text{III-6})$$

Thus, from III-6 and III-5,

$$\begin{aligned} \widetilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}^{(1)}(\underline{x}_2, \underline{v}_2, t) &= \frac{1}{N^2} \sum_{i=1}^N \sum_{j=1}^N F_i(\underline{x}_1, \underline{v}_1, t) F_j(\underline{x}_2, \underline{v}_2, t) \\ &= \frac{N-1}{N} \widetilde{F}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2, t) + \frac{1}{N^2} \sum_{i=1}^N F_i(\underline{x}_1, \underline{v}_1, t) F_i(\underline{x}_2, \underline{v}_2, t) \end{aligned} \quad (\text{III-7})$$

Since the last term of (III-7) is of order  $1/N$  compared to the other terms, we find that

$$\lim_{N \rightarrow \infty} \widetilde{F}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2, t) = \widetilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t) \widetilde{F}^{(1)}(\underline{x}_2, \underline{v}_2, t) \quad (\text{III-8})$$

We have therefore demonstrated the equivalence of the Hartree approximation and the ansatz II-82 in the limit of a many-body system. Note that III-8 could have been obtained for any N if the  $\psi_i$  in III-1 had all been equal. Physically, this is equivalent to describing each particle with the same generic wave function -- representing an average over the actual behavior of the N particles. For this reason, we refer to II-82 in general as a statistical Hartree approximation although it should be borne in mind that for large N it becomes equivalent to the Hartree approximation in the usual sense.

#### B. First Quantum Vlasov Equation

Proceeding now to an investigation of the consequences of II-82, we insert it into II-76 (with R=1) to obtain

$$\frac{\partial \widetilde{F}_{\alpha_1}^{(1)}}{\partial t} + \left\{ \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t), H^{(1)}(\underline{x}_1, \underline{v}_1, t) \right\}_{G.P.B}^{(1)} =$$

$$\frac{i}{\hbar} \left[ \exp \left[ -\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1} \right] - 1 \right] \left( (N-1) q^2 \sum_{\alpha_2=-S}^S \int d^3 \underline{x}_2 d^3 \underline{v}_2 \widetilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \phi(\underline{x}_1 - \underline{x}_2) \right) \left( \widetilde{F}_{\alpha_1}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right)$$

(III-9)

Since spin plays no role in this approximation, the spin indices are excess baggage. We therefore sum III-9 over  $\alpha_1$  and define

$$\widetilde{F}^{(1)} \equiv \sum_{\alpha_1=-S}^S \widetilde{F}_{\alpha_1}^{(1)}$$

(III-10)

Furthermore, recalling that

$$N \int d^3 \underline{v} \widetilde{F}^{(1)}(\underline{x}, \underline{v}, t) = \langle \rho(\underline{x}, t) \rangle$$

(III-11)

where  $\langle \rho(\underline{x}, t) \rangle$  is the (ensemble averaged) expectation value of the particle density at  $(\underline{x}, t)$ , we define the self-consistent field,  $\phi^{SCF}$  :

$$\phi^{SCF}(\underline{x}_1, t) = (N-1) \sum_{\alpha_2=-S}^S \int d^3x_2 d^3v_2 \tilde{F}_{\alpha_2}^{(1)}(\underline{x}_2, \underline{v}_2, t) \phi(\underline{x}_1 - \underline{x}_2) \quad (\text{III-12})$$

which, by virtue of III-11 is equivalent to

$$\phi^{SCF}(\underline{x}_1, t) = \frac{N-1}{N} \int d^3x_2 \langle \rho(\underline{x}_2, t) \rangle \phi(\underline{x}_1 - \underline{x}_2) \quad (\text{III-13})$$

We find, therefore, that III-9 when summed over  $\alpha_1$  can be written concisely as

$$\frac{\partial \tilde{F}^{(1)}}{\partial t} + \left\{ \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t), H_{SCF}(\underline{x}_1, \underline{v}_1, t) \right\}_{G.P.B.}^{(1)} = 0 \quad (\text{III-14})$$

where the self-consistent field Hamiltonian,  $H_{SCF}$ , is given by

$$H_{SCF}(\underline{x}_1, \underline{v}_1, t) \equiv \frac{1}{2} m v_1^2 + g^2 (\phi^{ext}(\underline{x}_1, t) + \phi^{SCF}(\underline{x}_1, t)) \quad (\text{III-15})$$

Finally, writing out the G.P.B. explicitly, we obtain the quantum analogue of the Vlasov equation\*, II-15,

$$\begin{aligned} \frac{\partial \tilde{F}^{(1)}}{\partial t} + \underline{v}_1 \cdot \nabla_{\underline{x}_1} \tilde{F}^{(1)} - \frac{1}{m} \nabla_{\underline{x}_1} g^2 (\phi^{ext} + \phi^{SCF}) \cdot \nabla_{\underline{v}_1} \tilde{F}^{(1)} - \left[ \frac{i\hbar}{2m} \nabla_{\underline{x}_1}^2 \tilde{F}^{(1)} \right. \\ \left. + \frac{ig^2}{\hbar} \sum_{n=2}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n (\phi^{ext} + \phi^{SCF})}{\partial x_1^k \partial x_1^l \dots} \frac{\partial^n \tilde{F}^{(1)}}{\partial v_1^k \partial v_1^l \dots} \right] = 0 \end{aligned} \quad (\text{III-16})$$

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\*In the next chapter we will derive another quantum analogue of the Vlasov equation based on the more realistic ansatz II-83 which will differ from III-16 in that additional ("exchange") terms occur within the brackets. We refer to the two cases as the first and second quantum Vlasov equations respectively.

An alternative form of III-16 is obtained by introducing the spatial Fourier transforms of  $\phi^{\text{ext}}$  and  $\phi^{\text{scF}}$  :

$$\phi^{\text{ext}}(\underline{x}, t) \equiv \frac{1}{(2\pi)^3} \int d^3q e^{i\underline{q} \cdot \underline{x}} f^{\text{ext}}(\underline{q}, t) \quad (\text{III-17})$$

$$\phi^{\text{scF}}(\underline{x}, t) \equiv \frac{1}{(2\pi)^3} \int d^3q e^{i\underline{q} \cdot \underline{x}} f^{\text{scF}}(\underline{q}, t) \quad (\text{III-18})$$

in which case III-16 becomes

$$\begin{aligned} \frac{\partial \widetilde{F}^{(n)}}{\partial t} + \underline{v}_i \cdot \underline{\nabla}_{\underline{x}_i} \widetilde{F}^{(n)} - \frac{i\hbar}{2m} \nabla_{\underline{x}_i}^2 \widetilde{F}^{(n)} - \frac{ig^2}{\hbar (2\pi)^3} \int d^3q e^{i\underline{q} \cdot \underline{x}_i} (f^{\text{ext}}(\underline{q}, t) + f^{\text{scF}}(\underline{q}, t)) \\ \times \left[ \widetilde{F}^{(n)}(\underline{x}_i, \underline{v}_i + \frac{\hbar}{m} \underline{q}, t) - \widetilde{F}^{(n)}(\underline{x}_i, \underline{v}_i, t) \right] = 0 \end{aligned} \quad (\text{III-19})$$

From this point on, a discussion of the physical significance and utility of III-16 would directly parallel that given for the classical case in Section II-B. In view of this redundancy, we need only sketch the general types of physical problems which can be fruitfully studied by means of this equation.

First, the time independent form of III-16, obtained by setting  $\partial \widetilde{F}^{(n)} / \partial t$  equal to zero, yields an equation that  $\widetilde{F}^{(n)}$  must satisfy if it is to represent a stationary ensemble. The characteristics of this equation for a given (time-independent)  $\phi^{\text{ext}}(\underline{x}_i)$  are the quantum analogues of the "constants of the motion" in the classical case, among which is the single particle energy in the self-consistent field. This quantity will differ from the classical expression II-19 in that an explicit dependence on the gradients of  $\phi^{\text{ext}}$  will occur by virtue of the bracketed terms in III-16. Any



functional of these characteristics will satisfy the time-independent form of III-16. Next, one appeals to a quantum-mechanical H-theorem or ensemble theory to determine this functional. Since this appeal goes beyond the content of III-16, there is no harm in introducing the appropriate quantum statistics at this point, even though it is not embodied in II-83. Thus, generally speaking, the time independent form of III-16, when augmented with a quantum-mechanical H-theorem, yields a description of the system in thermodynamic equilibrium. In the limit of zero temperature, one obtains an approximate description of the ground state. We defer further discussion of this class of problem to Chapter V where a specific case, the many-electron atom, is treated in some detail.

A second type of problem concerns the response of a system, initially in thermodynamic equilibrium, to a weak external field which varies in time at a rate large compared to the collision frequency. For systems with long-range interparticle forces, self-sustained collective modes of oscillation will be included in this category, appearing as poles in the response function. In Section C, we shall treat this case for an infinitely extended spatially homogeneous system.

Finally, at the opposite extreme where the system varies in time at a rate slow compared to the collision frequency, one assumes that local thermodynamic equilibrium is maintained by the collisions and obtains from III-16 the quantum analogue of the equations of inviscid hydrodynamics. This will be carried out in Section D.

C. Response of a Spatially Uniform System to Weak External Forces

Consider a system of  $N$  particles each having mass  $m$ , spin  $S$ , where the particle-particle interaction potential,  $g^2 \phi(\underline{x} - \underline{x}')$ , is given and has the Fourier transform:

$$\phi(\underline{x} - \underline{x}') \equiv \frac{1}{(2\pi)^3} \int d^3 q e^{i \underline{q} \cdot (\underline{x} - \underline{x}')} f(q) \quad (\text{III-20})$$

Let the system be exposed to an external field of the following form:

$$\phi^{\text{ext}}(\underline{x}, t) = \phi_V^{\text{ext}}(\underline{x}) + \beta \phi_I^{\text{ext}}(\underline{x}, t) \quad (\text{III-21})$$

where  $\phi_V^{\text{ext}}$  is a static field\* which confines the particles to a volume in such a fashion that the particle number density,  $n$ , within  $V$  is spatially uniform for  $t < 0$ .  $\beta \phi_I^{\text{ext}}(\underline{x}, t)$  represents an arbitrary additional field which is switched on at  $t = 0$ , whose strength is characterized by the dimensionless number  $\beta$ . Assume that  $N$  and  $V$  are sufficiently large that surface effects can be ignored so that for all intents and purposes the system can be regarded as spatially infinite with finite constant density  $n$ . For  $t < 0$  the system is assumed to be in thermal equilibrium at some temperature  $T$ . We wish to find  $\tilde{F}^{(1)}$  for this problem.

For  $t < 0$ ,  $\phi^{\text{ext}} + \phi^{\text{scF}}$  is (by the definition of  $\phi_V^{\text{ext}}$ ) spatially constant so that III-16 reduces to

$$\frac{\partial \tilde{F}^{(1)}}{\partial t} + \underline{v} \cdot \nabla_{\underline{x}} \tilde{F}^{(1)} = 0 \quad t < 0 \quad (\text{III-22})$$

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\*In the case where the system in question consists of the free electrons in a fully ionized plasma or the conduction electrons in a metal, for example,  $\phi_V^{\text{ext}}$  represents the smeared out effect of the ions or lattice respectively.

Therefore, any  $\tilde{F}^{(1)}$  which does not depend on  $\underline{x}$  will be constant in time and hence characterizes a stationary ensemble. Since we have assumed that the system is initially in thermodynamic equilibrium at temperature T, we describe it by means of a quantum-mechanical macrocanonical ensemble and find from any text on statistical mechanics that

$$\tilde{F}_{t < 0}^{(1)} \equiv \frac{F_0(v)}{N} = \frac{1}{N} \left[ \frac{(2S+1)}{(2\pi)^3} \frac{m^3}{h^3} \left[ \exp\left(\frac{\frac{1}{2}mv^2 + \mu(n,T)}{kT}\right) \pm 1 \right]^{-1} \right] \quad (\text{III-23})$$

where the + sign is chosen if S is half integral, - if integral and  $\mu(n,T)$  is determined by the normalization condition

$$N \int \tilde{F}_{t < 0}^{(1)}(v) d^3v \equiv \int F_0(v) d^3v = n \quad (\text{III-24})$$

For  $t \geq 0$ , let

$$\tilde{F}^{(1)}(\underline{x}, v, t) \equiv \frac{1}{N} F_0(v) + \frac{1}{N} \beta F_1(\underline{x}, v, t) \quad t \geq 0 \quad (\text{III-25})$$

so that  $F_1$  represents the departure from the equilibrium distribution caused by the perturbing potential  $\phi_1^{\text{ext}}(\underline{x}, t)$ . The self-consistent field,  $\phi_1^{\text{scF}}(\underline{x}, t)$ , due to  $F_1$  is given by (III-12)

$$\beta \phi_1^{\text{scF}}(\underline{x}, t) = \beta \int d^3x' d^3v F_1(\underline{x}', v, t) \phi(\underline{x} - \underline{x}') \quad (\text{III-26})$$

Using the form III-19 for the quantum Vlasov equation, we find that  $F_1$  satisfies the equation

$$\begin{aligned} \beta \frac{\partial F_1}{\partial t} + \beta \underline{v} \cdot \nabla_{\underline{x}} F_1 - \frac{i\hbar}{2m} \beta \nabla_{\underline{x}}^2 F_1 - \frac{i q^2 \beta}{\hbar (2\pi)^3} \int d^3q e^{i\underline{q} \cdot \underline{x}} \left( f_1^{\text{ext}}(\underline{q}, t) + f_1^{\text{scF}}(\underline{q}, t) \right) \\ \times \left[ \left( F_0(\underline{v} + \frac{\hbar \underline{q}}{m}) - F_0(\underline{v}) \right) + \beta \left( F_1(\underline{x}, \underline{v} + \frac{\hbar \underline{q}}{m}, t) - F_1(\underline{x}, \underline{v}, t) \right) \right] = 0 \end{aligned} \quad (\text{III-27})$$



where  $f_1^{\text{ext}}$  and  $f_1^{\text{scF}}$  are the spatial Fourier transforms (III-17 and III-18) of  $\phi_1^{\text{ext}}$  and  $\phi_1^{\text{scF}}$ , and  $F_1$  has the initial value

$$F_1(\underline{x}, \underline{v}, t) = 0 \quad t \leq 0 \quad (\text{III-28})$$

For weak fields (i.e.  $\beta \ll 1$ ) we ignore the term quadratic in  $\beta$  to obtain the linearized equation

$$\begin{aligned} \frac{\partial F_1}{\partial t} + \underline{v} \cdot \nabla_{\underline{x}} F_1 - \frac{i\hbar}{2m} \nabla_{\underline{x}}^2 F_1 - \frac{ig^2}{\hbar(2\pi)^3} \int d\underline{q} e^{i\underline{q} \cdot \underline{x}} (f_1^{\text{ext}}(\underline{q}, t) + f_1^{\text{scF}}(\underline{q}, t)) \\ \times [F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v})] = 0 \end{aligned} \quad (\text{III-29})$$

To solve this equation, we introduce the following Fourier transforms:

$$F_1(\underline{x}, \underline{v}, t) \equiv \frac{1}{(2\pi)^4} \int d\underline{q} \int_{-\infty}^{\infty} d\omega e^{i(\underline{q} \cdot \underline{x} - \omega t)} \mathcal{F}(\underline{q}, \underline{v}, \omega) \quad (\text{III-30})$$

$$f_1^{\text{ext}}(\underline{q}, t) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} f_1^{\text{ext}}(\underline{q}, \omega) \quad (\text{III-31})$$

$$f_1^{\text{scF}}(\underline{q}, t) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega e^{-i\omega t} f_1^{\text{scF}}(\underline{q}, \omega) \quad (\text{III-32})$$

in terms of which III-29 becomes

$$(-i\omega + i\underline{v} \cdot \underline{q} + \frac{i\hbar}{2m} \underline{q}^2) \mathcal{F}_1 - \frac{ig^2}{\hbar} [F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v})] (f_1^{\text{ext}}(\underline{q}, \omega) + f_1^{\text{scF}}(\underline{q}, \omega)) = 0 \quad (\text{III-33})$$

Furthermore, due to III-26 and III-20 we have

$$f_1^{\text{scF}}(\underline{q}, \omega) = f(\underline{q}) \int d\underline{v} \mathcal{F}_1(\underline{q}, \underline{v}, \omega) \quad (\text{III-34})$$



Equations III-33 and III-34 are easily solved to yield the desired result.

$$\mathcal{F}(q, \nu, \omega) = \frac{g^2}{\hbar} [F_0(\nu + \frac{\hbar q}{m}) - F_0(\nu)] b_1^{ext}(q, \omega)$$


---


$$(-\omega - i\epsilon + \nu \cdot q + \frac{\hbar q^2}{2m}) \left\{ 1 - \frac{g^2}{\hbar} f(q) \int d^3 \nu' \frac{[F_0(\nu' + \frac{\hbar q}{m}) - F_0(\nu')]}{-\omega - i\epsilon + \nu' \cdot q + \frac{\hbar q^2}{2m}} \right\}$$

(III-35)

where  $\epsilon$  is a positive infinitesimal arising from causality (i.e. III-28).

III-35 and III-23 solve the problem.

We observe that the response function becomes singular if

$$-\omega + \nu \cdot q + \frac{\hbar q^2}{2m} = 0 ; \quad F_0(\nu + \frac{\hbar q}{m}) - F_0(\nu) \neq 0$$

(III-36)

or

$$\left\{ 1 - \frac{g^2}{\hbar} f(q) \int d^3 \nu' \frac{[F_0(\nu' + \frac{\hbar q}{m}) - F_0(\nu')]}{-\omega - i\epsilon + \nu' \cdot q + \frac{\hbar q^2}{2m}} \right\} = 0$$

(III-37)

which therefore correspond to modes of excitation of the system. III-36 describes single particle excitations (and de-excitations) where a particle of momentum  $m\nu$  is scattered into the momentum state  $(m\nu + \hbar q)$  with a change in energy  $\hbar\omega$ . III-37 is the dispersion relation for collective oscillations of the system brought about by the interparticle interaction  $f(q)$ . The vanishing of the real part of the bracketed term gives the location of these modes in the  $\omega, q$  plane. The imaginary part, obtained by means of the identity

$$\lim_{\epsilon \rightarrow 0} \frac{1}{x + i\epsilon} = P\left(\frac{1}{x}\right) - i\pi \delta(x)$$

(III-38)

yields the lifetime of these excitations. For a system with Coulomb interactions:

$$g^2 = e^2$$

$$f(q) = \frac{4\pi}{q^2} \quad (\text{III-39})$$

III-37 is the quantum-mechanical dispersion relation for plasma oscillations. It is easily shown that in the classical limit, the real part gives the ordinary plasma dispersion relation and the imaginary part gives the so-called "Landau" damping (29a)

Of particular interest is the zero-temperature electron gas in which case

$$F_0(v) = \frac{1}{4\pi^3} \frac{m^3}{\hbar^3} \begin{cases} 1 & v \leq v_f \\ 0 & v > v_f \end{cases} \quad (\text{III-40})$$

where the Fermi velocity,  $v_f$ , is related to the density by

$$v_f = \left( \frac{3n}{\pi} \right)^{1/3} \frac{\pi \hbar}{m} \quad (\text{III-41})$$

Introducing III-38 - III-41 in III-37 yields after some algebra

$$\left\{ 1 - \frac{e^2 m^2}{\pi^2 \hbar^3} \oint_{(v' \leq v_f)} d^3 v' \left[ (\omega - \underline{v}' \cdot \underline{q})^2 - \left( \frac{\hbar q^2}{2m} \right)^2 \right]^{-1} \right.$$

$$\left. + \frac{i e^2 m^3}{\pi \hbar^4 q^2} \int_{\left( \begin{smallmatrix} v' \leq v_f \\ |\underline{v}' + \frac{\hbar}{m} \underline{q}| > v_f \end{smallmatrix} \right)} d^3 v' \left[ \delta(\omega - \underline{v}' \cdot \underline{q} - \frac{\hbar q^2}{2m}) - \delta(\omega + \underline{v}' \cdot \underline{q} + \frac{\hbar q^2}{2m}) \right] \right\} = 0 \quad (\text{III-42})$$

This is seen to be just the Bohm-Pines (30) "plasmon" dispersion relation which is extensively discussed in the literature (31). The left-hand side of III-42, which can be shown to be identifiable with the frequency and wave-number dependent dielectric constant for the system, is identical to the dielectric constant as computed in the so-called Random Phase Approximation (R.P.A.) by Nozieres and Pines (32). It was first obtained by Lindhard (33) from time-dependent perturbation theory.

It should be emphasized that the general result III-35 is only applicable for times short compared to the collision time or equivalently, for frequencies large compared to the collision frequency.

#### D. Quantum Hydrodynamics

Within the context of the neglect of exchange effects, the exact equation for  $\tilde{F}^{(i)}$  can be formally written as

$$\frac{\partial \tilde{F}^{(i)}}{\partial t} + \left\{ \tilde{F}^{(i)}, H_{scF}^{(i)} \right\}_{G.P.B.}^{(i)} = \left( \frac{\partial \tilde{F}^{(i)}}{\partial t} \right)_{\text{collisions}} \quad (\text{III-43})$$

where the left-hand side is that of quantum Vlasov equation III-14, and the right-hand side represents the effect of all dynamic collision processes. If we imagine configuration space to be divided in cells each of which has linear dimensions large compared to the collision "mean free path", then from the fact that the collision process\* conserves number of particles, momentum and energy we observe that macroscopic conservation laws for these

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\*Recall that it was initially assumed that the particles have no internal degrees of freedom. Furthermore, we assumed that the effect of objects external to the system can be represented as a scalar, velocity-independent potential,  $\phi^{ext}$ . Thus, such processes as electron-ion collisions in a plasma or electron-phonon interactions in a metal lie outside the scope of the present discussion.



quantities (which apply to the whole of each such "coarse-grained" cell) can be derived from III-14, since the contribution of the collision term is zero. In the classical situation, for example, it is well known that the first three velocity-space moments of the Vlasov equation yield respectively the continuity equations for mass, momentum and energy. We wish to derive the corresponding equations from the quantum Vlasov equation.

We proceed from III-16 written in the form

$$\begin{aligned} \frac{\partial \tilde{F}^{(0)}}{\partial t} + v^k \frac{\partial \tilde{F}^{(0)}}{\partial x^k} - \frac{q^2}{m} \frac{\partial \phi_T}{\partial x^k} \frac{\partial \tilde{F}^{(0)}}{\partial v^k} - \left[ \frac{i\hbar}{2m} \frac{\partial^2 \tilde{F}^{(0)}}{\partial x^k \partial x^k} \right. \\ \left. + \frac{ig^2}{\hbar} \sum_{n=2}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n \phi_T}{\partial x^k \partial x^k \dots} \frac{\partial^n \tilde{F}^{(0)}}{\partial v^k \partial v^k \dots} \right] = 0 \end{aligned} \quad (\text{III-44})$$

where the repeated Cartesian indices  $k, l, \dots$  are understood to be summed from 1 to 3 and

$$\phi_T(x, t) \equiv \phi^{\text{ext}}(x, t) + \phi^{\text{scF}}(x, t) \quad (\text{III-45})$$

Integrating III-44 over all velocity space, and integrating by parts where necessary yields

$$\frac{\partial}{\partial t} \left[ \int d^3v \tilde{F}^{(0)} \right] + \nabla \cdot \left[ \int d^3v v \tilde{F}^{(0)} - \frac{i\hbar}{2m} \nabla \int d^3v \tilde{F}^{(0)} \right] = 0 \quad (\text{III-46})$$

Next multiplying III-44 by  $mv^M$  ( $M=1,2,3$ ) and integrating over velocity space leads in a similar fashion to the vector equation with components

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \int d^3v m v^M \tilde{F}^{(0)} \right] + \frac{\partial}{\partial x^k} \left[ \int d^3v m v^k v^M \tilde{F}^{(0)} - \frac{i\hbar}{2} \frac{\partial}{\partial x^k} \int d^3v v^M \tilde{F}^{(0)} \right] \\ + \frac{q^2}{m} \frac{\partial \phi_T}{\partial x^M} \left[ \int d^3v \tilde{F}^{(0)} \right] = 0 \end{aligned} \quad (\text{III-47})$$

( $M=1,2,3$ )



Finally, multiplying by  $\frac{1}{2} m v^2$  and integrating over velocity space gives the scalar equation

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \int d^3v \frac{1}{2} m v^2 \tilde{F}^{(0)} \right] + \nabla \cdot \left[ \int d^3v \underline{v} \left( \frac{1}{2} m v^2 \right) \tilde{F}^{(0)} - \frac{i \hbar}{2m} \nabla \int d^3v \left( \frac{1}{2} m v^2 \right) \tilde{F}^{(0)} \right] \\ + g^2 \nabla \phi_T \cdot \left[ \int d^3v \underline{v} \tilde{F}^{(0)} \right] + \frac{i g^2 \hbar}{2m} (\nabla^2 \phi_T) \left[ \int d^3v \tilde{F}^{(0)} \right] = 0 \end{aligned} \quad (\text{III-48})$$

It is now necessary to relate the bracketed quantities in these equations to the expectation values of physical observables. This is a simple matter for the quantity  $\int \tilde{F}^{(0)} d^3v$ , which by virtue of II-35 is just

$$\int \tilde{F}^{(0)} d^3v = \frac{\langle n(\underline{x}, t) \rangle}{N} \quad (\text{III-49})$$

where  $\langle n \rangle$  is the (ensemble averaged) expectation value of the particle (number) density at  $(\underline{x}, t)$  and  $N^{-1}$  arises from our choice of normalization. Since this  $N^{-1}$  factor will occur in every term and thus can be divided out of III-46 - III-48, we will henceforth ignore it.

The remaining bracketed terms cannot be treated so simply, and we must go back to the basic theorem II-44. Consider first the classical expression

$$\underline{p}(\underline{x}') \equiv m \underline{v} \delta(\underline{x} - \underline{x}') \quad (\text{III-50})$$

which, when integrated over all of phase space with the classical distribution function  $F(\underline{x}, \underline{v})$ , gives the average value of the momentum at the point  $\underline{x}'$ . The quantum-mechanical Hermitean operator which in configuration

space corresponds to the function III-50 is

$$\mathcal{P} = \frac{1}{2} \left[ \delta(\underline{x} - \underline{x}') \frac{\hbar}{i} \nabla_{\underline{x}} + \frac{\hbar}{i} \nabla_{\underline{x}} \delta(\underline{x} - \underline{x}') \right] \quad (\text{III-51})$$

This is now written in "anti well-ordered" form (see p. 29) by performing the necessary commutations:

$$\mathcal{P} = \frac{\hbar}{i} \nabla_{\underline{x}} \delta(\underline{x} - \underline{x}') + \left[ \frac{i\hbar}{2} (\nabla_{\underline{x}} \delta(\underline{x} - \underline{x}')) \right] \quad (\text{III-52})$$

Thus, from II-44, the phase space function

$$\mathcal{P}(\underline{x}', \underline{v}) = m \underline{v} \delta(\underline{x} - \underline{x}') + \frac{i\hbar}{2} (\nabla_{\underline{x}} \delta(\underline{x} - \underline{x}')) \quad (\text{III-53})$$

when integrated over all of phase space with  $\tilde{F}^{(0)}$  will yield the quantum mechanical expectation value of the operator III-51 which in turn corresponds to a measurement of the momentum at  $\underline{x}'$ . Performing this integration, we find

$$\int d^3v \underline{v} \tilde{F}^{(0)}(\underline{x}, \underline{v}, t) - \frac{i\hbar}{2m} \nabla_{\underline{x}} \int d^3v \tilde{F}^{(0)}(\underline{x}, \underline{v}, t) = \frac{1}{m} \langle \mathcal{P}(\underline{x}, t) \rangle \quad (\text{III-54})$$

where  $\langle \mathcal{P}(\underline{x}, t) \rangle$  is the (ensemble averaged) quantum mechanical expectation value of the momentum at  $(\underline{x}, t)$ . With the definition

$$\frac{1}{m} \langle \mathcal{P} \rangle \equiv \langle n \rangle \langle \underline{u} \rangle \quad (\text{III-55})$$

where  $\langle \underline{u} \rangle$  is the convective or "drift" velocity, III-46 becomes

$$\frac{\partial}{\partial t} \langle n \rangle + \nabla \cdot (\langle n \rangle \langle \underline{u} \rangle) = 0 \quad (\text{III-56})$$

which is identical to the classical mass continuity equation.

In equation III-47, another integral

$$\int d^3v \, m \, v^k v^M \tilde{F}^{(0)} \quad (\text{III-57})$$

occurs which must be similarly treated. The classical tensor  $\Pi$  with elements

$$T^{KM} \equiv \delta(\underline{x} - \underline{x}') \, m \, v^k v^M \quad (\text{III-58})$$

when integrated over phase space with the classical distribution function gives the total "stress tensor" at the point  $\underline{x}'$ . The quantum-mechanical Hermitean operator analogue of III-58 is

$$\Pi^{KM} = \frac{1}{2m} \left( \delta(\underline{x} - \underline{x}') \left( \frac{\hbar}{i} \right)^2 \frac{\partial^2}{\partial x^k \partial x^M} + \left( \frac{\hbar}{i} \right)^2 \frac{\partial^2}{\partial x^k \partial x^M} \delta(\underline{x} - \underline{x}') \right) \quad (\text{III-59})$$

which in anti well-ordered form becomes

$$\begin{aligned} \Pi^{KM} = & \frac{1}{m} \left( \frac{\hbar}{i} \right)^2 \frac{\partial^2}{\partial x^k \partial x^M} \delta(\underline{x} - \underline{x}') + \frac{i\hbar}{2m} \left( \frac{\hbar}{i} \right) \frac{\partial}{\partial x^M} \left( \frac{\partial}{\partial x^k} \delta(\underline{x} - \underline{x}') \right) \\ & + \frac{i\hbar}{2m} \left( \frac{\hbar}{i} \right) \frac{\partial}{\partial x^k} \left( \frac{\partial}{\partial x^M} \delta(\underline{x} - \underline{x}') \right) - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^k \partial x^M} \delta(\underline{x} - \underline{x}') \right) \end{aligned} \quad (\text{III-60})$$

Thus, from II-44, the phase space function

$$\begin{aligned} T^{KM} = & m \, v^k v^M \delta(\underline{x} - \underline{x}') + \frac{i\hbar}{2} v^M \left( \frac{\partial}{\partial x^k} \delta(\underline{x} - \underline{x}') \right) \\ & + \frac{i\hbar}{2} v^k \left( \frac{\partial}{\partial x^M} \delta(\underline{x} - \underline{x}') \right) - \frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^k \partial x^M} \delta(\underline{x} - \underline{x}') \right) \end{aligned} \quad (\text{III-61})$$

when integrated with  $\tilde{F}^{(1)}$  yields the expectation value of III-59. Performing



the integration gives

$$\int d^3v m v^k v^M \tilde{F}^{(1)}(\underline{x}, \underline{v}, t) - \frac{i\hbar}{2} \frac{\partial}{\partial x^k} \int d^3v v^M \tilde{F}(\underline{x}, \underline{v}, t) \\ - \frac{i\hbar}{2} \frac{\partial}{\partial x^M} \int d^3v v^k \tilde{F}(\underline{x}, \underline{v}, t) - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^k \partial x^M} \int d^3v \tilde{F}(\underline{x}, \underline{v}, t) = \langle T^{KM}(\underline{x}, t) \rangle \quad (\text{III-62})$$

where  $\langle T^{KM}(\underline{x}, t) \rangle$  is the (ensemble averaged) expectation value of the total stress tensor at  $(\underline{x}, t)$ .

Introducing III-62, III-54 and III-55 into III-47 and making use of III-56 gives finally

$$\frac{\partial}{\partial t} (m \langle n \rangle \langle \underline{u} \rangle) + \underline{\nabla} \cdot \langle \underline{\Pi} \rangle + \langle n \rangle \underline{\nabla} g^2 \phi_T + \frac{\hbar^2}{4m} \underline{\nabla} (\nabla^2 \langle n \rangle) = 0 \quad (\text{III-63})$$

where the elements at the tensor  $\underline{\Pi}$  are given in III-62.

This is the momentum continuity equation. The first three terms are recognized to be just the usual classical expression. The last term represents the quantum correction to this equation.

Deferring for a moment the consideration of III-48, we now introduce the underlying assumption of hydrodynamics: The system is assumed to vary in time sufficiently slowly to allow collisions to establish local thermodynamic equilibrium. This means that if we locally transform to a reference frame moving with the drift velocity  $\langle \underline{u}(\underline{x}, t) \rangle$  then in this frame,  $\tilde{F}^{(1)}$  is the solution of the time-independent quantum Vlasov equation appropriate to a (quantum) macrocanonical ensemble characterized by the local



temperature  $T(x, t)$  and density  $\langle n(x, t) \rangle$ . Specifically, let  $\tilde{F}^{(0) \prime}$  be the solution of

$$\left\{ \tilde{F}^{(0) \prime}(x, v, t), H_{scF}^{(0)}(x, v, t) \right\}_{G.P.B.}^{(1)} = 0 \quad (\text{III-64})$$

appropriate to this ensemble, with

$$\int d^3v \tilde{F}^{(0) \prime}(x, v, t) = \langle n(x, t) \rangle \quad (\text{III-65})$$

Then, the ansatz of local thermodynamic equilibrium takes the form

$$\text{Re } \tilde{F}^{(0)}(x, v, t) = \text{Re } \tilde{F}^{(0) \prime}(x, v - \langle u(x, t) \rangle, t) \quad (\text{III-66})$$

where  $\text{Re } \tilde{F}^{(0) \prime}$  is now a known function.\* The real part is taken because it is only necessary that the observable local properties (which by the basic theorem II-45 are contained in  $\text{Re } \tilde{F}$ ) should transform according to III-66.

By means of III-66, the  $\nabla \cdot \langle \pi \rangle$  term in III-63 can now be expressed in terms of  $\langle n \rangle$ ,  $\langle u \rangle$  and quantities calculable from  $\text{Re } \tilde{F}^{(0) \prime}$ . To

\*In Chapter V we shall find from a perturbation expansion in powers of  $\hbar$  that to order  $\hbar^2$  and neglecting exchange:

$$\begin{aligned} \text{Re } \tilde{F}^{(0) \prime}(x, v, t) = & \left[ F_0(\epsilon) - \frac{\hbar^2}{4m} (\nabla^2 g^2 \phi_T) \frac{d^2 F_0}{d\epsilon^2} - \frac{\hbar^2}{6} (v \cdot \nabla v \cdot \nabla g^2 \phi_T \right. \\ & \left. + \frac{1}{m} (\nabla g^2 \phi_T)^2) \frac{d^3 F_0}{d\epsilon^3} - \frac{\hbar^2}{8} (v \cdot \nabla g^2 \phi_T)^2 \frac{d^4 F_0}{d\epsilon^4} \right]_{\epsilon = \frac{1}{2} m v^2 + \phi_T} \end{aligned} \quad (\text{III-67})$$

where

$$F_0(\epsilon) = \frac{(2S+1)}{(2\pi)^3} \frac{m^3}{\hbar^3} \left[ \exp\left(\frac{\epsilon + \psi(x, t)}{\hbar T(x, t)}\right) \pm 1 \right]^{-1} \quad (\text{III-68})$$

and  $\psi$  is determined from III-65.

this end, we first take the real and imaginary parts of III-54 to obtain (using III-65 and III-66)

$$\int d^3w \, \underline{w} \, R_e \, \tilde{F}^{(0)'}(\underline{x}, \underline{w}, t) = 0 \quad (\text{III-69})$$

and

$$dm \int d^3v \, \underline{v} \, \tilde{F}^{(0)}(\underline{x}, \underline{v}, t) = \frac{\hbar}{2m} \underline{\nabla} \langle n \rangle \quad (\text{III-70})$$

Next, taking the real and imaginary parts of III-62 and making use of III-66, III-69 and III-70 gives

$$\langle T^{KM}_{(\underline{x}, t)} \rangle = \langle T'^{KM}_{(\underline{x}, t)} \rangle + m \langle u^K_{(\underline{x}, t)} \rangle \langle u^M_{(\underline{x}, t)} \rangle \langle n_{(\underline{x}, t)} \rangle \quad (\text{III-71})$$

and

$$dm \int d^3v \, m v^K v^M \tilde{F}^{(0)}(\underline{x}, \underline{v}, t) = \frac{\hbar}{2} \left[ \frac{\partial}{\partial x^K} \langle n \rangle \langle u^M \rangle + \frac{\partial}{\partial x^M} \langle n \rangle \langle u^K \rangle \right] \quad (\text{III-72})$$

where

$$\langle T'^{KM}_{(\underline{x}, t)} \rangle \equiv R_e \int d^3w \, m w^K w^M \tilde{F}^{(0)'}(\underline{x}, \underline{w}, t) \quad (\text{III-73})$$

and by virtue of II-45 is identified with the (ensemble averaged) expectation value of the local kinetic stress tensor as computed in the moving (Lagrangian) frame.

Introducing III-71 into III-63 gives, after some manipulation, the final form of the momentum equation:

$$\begin{aligned} m \langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \langle \underline{u} \rangle + \underline{\nabla} \cdot \langle \underline{\pi}' \rangle + \langle n \rangle \underline{\nabla} g^2 \phi_r \\ + \frac{\hbar^2}{4m} \underline{\nabla} (\nabla^2 \langle n \rangle) = 0 \end{aligned} \quad (\text{III-74})$$

In this equation, it is understood that the kinetic stress tensor  $\langle \Pi' \rangle$  is to be expressed in terms of  $\langle n \rangle$ ,  $T$  and  $\phi_T$  by means of an explicit form for  $\text{Re } \tilde{F}'^{(0)}$  (such as III-67), and, furthermore, that  $\phi_T$  is related to  $\langle n \rangle$  via

$$\phi_T(\underline{x}, t) = \phi^{\text{ext}}(\underline{x}, t) + \int d^3x' \langle n(\underline{x}', t) \rangle \phi(\underline{x} - \underline{x}') \quad (\text{III-75})$$

Turning finally to the energy equation, we take the real part of III-48 and, making use of the foregoing relations, obtain after some manipulation\* the result

$$\begin{aligned} m \langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \left( \langle \bar{\epsilon}' \rangle^{\text{kin}} - \frac{\hbar^2}{4m^2 \langle n \rangle} \nabla^2 \langle n \rangle \right) + \langle \Pi' \rangle \cdot \underline{\nabla} \langle \underline{u} \rangle \\ + \frac{\hbar^2}{4m} (\nabla^2 \langle n \rangle) \underline{\nabla} \cdot \langle \underline{u} \rangle + \underline{\nabla} \cdot \langle \underline{Q}' \rangle = 0 \end{aligned} \quad (\text{III-76})$$

where the (ensemble averaged) expectation value of the kinetic energy per unit mass is defined by

$$\begin{aligned} \langle \bar{\epsilon}'(\underline{x}, t) \rangle^{\text{kin}} &\equiv \frac{1}{m \langle n(\underline{x}, t) \rangle} \text{Re} \int d^3w \frac{1}{2} m w^2 \tilde{F}'^{(0)}(\underline{x}, \underline{w}, t) \\ &= \frac{1}{2m \langle n \rangle} \text{Trace } \langle \Pi' \rangle \end{aligned} \quad (\text{III-77})$$

and the (ensemble averaged) expectation value of the thermal current is

$$\langle \underline{Q}'(\underline{x}, t) \rangle \equiv \text{Re} \int d^3w \underline{w} \left( \frac{1}{2} m w^2 \right) \tilde{F}'^{(0)}(\underline{x}, \underline{w}, t) \quad (\text{III-78})$$

Now one can show quite generally from the form of III-64 and the fact that when  $\hbar \rightarrow 0$ ,  $\tilde{F}'^{(0)}$  must be real that the real part of  $\tilde{F}'^{(0)}$  is unchanged by

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\* See Appendix B



a reflection in velocity space and consequently that  $\langle \mathcal{Q}' \rangle$  vanishes. We formally retain it in III-76 for reasons to be discussed presently.

In the Hartree approximation, therefore, the equations of inviscid isentropic hydrodynamics are III-56, III-64, III-74 and III-76 (with  $\langle \mathcal{Q}' \rangle = 0$ ). It is important to note that these equations differ from the classical case in two respects. First, there are the new terms depending explicitly on  $\hbar^2$ , which arise because the simultaneous specification of particle position and velocity implicit in hydrodynamical equations violates the uncertainty principle. Thus in III-74, the last term represents a zero point pressure which must be added to the expectation value of the kinetic stresses when density gradients exist. Similarly III-76 states that only the excess of kinetic energy over and above a zero point energy can be taken to represent heat.

In addition to these explicit quantum corrections, further modifications arise from the fact that  $\langle \pi' \rangle$  and  $\langle \bar{\epsilon}' \rangle^{\text{kin}}$  are related to  $\langle n \rangle$  and gradients of  $\phi_T$  (i.e. the equation of state) via the quantum mechanical equation III-64 for  $\tilde{F}^{(0)}$ . One can see from III-67, for example, that the equation of state will be modified by terms of order  $\hbar^2$  when external forces act on the system.

The exact equations of hydrodynamical transport will depart from the foregoing in two ways. First, irreversible effects will enter when collisions are properly taken into account (i.e. by adding to III-44 the quantum-mechanical collision integral and abandoning III-66). As in the classical case, we expect that this deficiency can be approximately remedied



by adding to the kinetic stress tensor  $\langle \Pi \rangle$ , a viscous stress tensor,  $\langle \nabla \rangle$ , given by

$$\langle \nabla \rangle \equiv -\eta \nabla \langle u \rangle \quad (\text{III-79})$$

where  $\eta$  is a phenomenological coefficient, and further, by introducing entropy production via

$$\langle \mathcal{Q}' \rangle \equiv -\alpha \nabla \phi_T - \kappa \nabla T \quad (\text{III-80})$$

When long range interparticle forces exist, a second modification due to exchange effects must also be made. In the next chapter, we will introduce the Hartree-Fock approximation, from which the second quantum Vlasov equation will be derived. Velocity space moments of this equation will then lead to the correct equations of inviscid isentropic hydrodynamics. Our motivation for having derived the admittedly incomplete hydrodynamical equations of this section is that exchange effects beyond those included in the use of quantum statistical ensembles (i.e. III-68) are often unimportant so that the foregoing equations should be a good approximation in those cases. Furthermore, it is instructive to see what new consequences are brought in at each stage of approximation to the many-body theory. Finally, it should be emphasized that the results of the present chapter, being derivable equally easily from the Wigner distribution function, do not represent a demonstration of any intrinsic merit of an approach based on the von Roos q.m.d.f. This will no longer be the case when we go to the Hartree-Fock approximation.

# Chapter IV     The Hartree-Fock Approximation

## A. General Remarks

As in the previous chapter, our first objective is to investigate the form of the N-particle wave function (for a pure case) which is implied by the ansatz II-83. This step is not, of course, essential to the logical development of the theory and is taken primarily for the purpose of establishing contact with conventional approximation procedures. For reasons of simplicity, we shall limit this discussion to the case of particles with spin zero and spin 1/2.

In the latter instance, consider a system of N spin 1/2 particles in an energy eigenstate, E, whose total spin projection in the +Z direction is (m-p) 1/2 where  $m \geq p$  and  $m + p = N$ . The so-called Hartree-Fock (34) approximation is characterized by the assumption that the N particle wave function  $\Psi^{(N)}$  can be represented as a single Slater determinant of single particle space and spin wave functions with the specific form

$$\Psi_{(1, \dots, N)}^{(N)} = \text{const } e^{\frac{iEt}{\hbar}} \begin{vmatrix} u_1(x_1) \xi_{1/2}^{(1)} & \dots & u_1(x_N) \xi_{1/2}^{(N)} \\ \vdots & & \vdots \\ u_m(x_1) \xi_{1/2}^{(1)} & \dots & u_m(x_N) \xi_{1/2}^{(N)} \\ w_1(x_1) \xi_{-1/2}^{(1)} & \dots & w_1(x_N) \xi_{-1/2}^{(N)} \\ \vdots & & \vdots \\ w_p(x_1) \xi_{-1/2}^{(1)} & \dots & w_p(x_N) \xi_{-1/2}^{(N)} \end{vmatrix} \quad (\text{IV-1})$$

where the functions  $\xi_{1/2}(i)$  and  $\xi_{-1/2}(i)$  are "up" and "down" spinors respectively, henceforth to be denoted simply as  $\uparrow_i$  and  $\downarrow_i$ . From the properties of determinants, non-triviality of  $\Psi^{(N)}$  demands that the functional sets  $\{u_i\}$  and  $\{w_i\}$  be individually linearly independent. Aside from this requirement, the functions  $u_i$  and  $w_i$  are arbitrary.\*

We first observe that without loss of generality, the  $\{u_i\}$  and  $\{w_i\}$  may be taken to orthonormal:

$$\begin{aligned} \int d^3x u_i(x) u_j(x) &= \delta_{ij} \\ \int d^3x w_i(x) w_j(x) &= \delta_{ij} \end{aligned} \quad (\text{IV-2})$$

This follows from the fact that by virtue of the linear independence of the  $\{u_i\}$  and  $\{w_i\}$ , orthonormal sets  $\{u'_i\}$  and  $\{w'_i\}$  can be constructed from linear combinations of  $\{u_i\}$  and  $\{w_i\}$  by the Schmidt procedure. Inverting this transformation, one has in general

$$\begin{aligned} u_i(x) &= \sum_{j=1}^m c_{ij} u'_j(x) \\ w_i(x) &= \sum_{j=1}^p d_{ij} w'_j(x) \end{aligned} \quad (\text{IV-3})$$

which when inserted into IV-1 gives

$$\Psi_{(1, \dots, N)}^{(N)} = \pm \text{const} e^{\frac{iEt}{\hbar}} \left[ \prod_{i=1}^m \sum_{j=1}^m c_{ij} \right] \left[ \prod_{k=1}^p \sum_{l=1}^p d_{kl} \right] \begin{vmatrix} u'_1(x_1) \uparrow_1 & \dots & u'_1(x_N) \uparrow_N \\ \vdots & & \vdots \\ u'_m(x_1) \uparrow_1 & \dots & u'_m(x_N) \uparrow_N \\ w'_1(x_1) \downarrow_1 & \dots & w'_1(x_N) \downarrow_N \\ \vdots & & \vdots \\ w'_p(x_1) \downarrow_1 & \dots & w'_p(x_N) \downarrow_N \end{vmatrix} \quad (\text{IV-4})$$

\*A "restricted" Hartree-Fock scheme in which  $m = p$  and  $u_i = w_i$  ( $i=1, \dots, m$ ) is often used as an approximation to the ground state of a normal many-fermion system.



where use has been made of the fact that the magnitude of a determinant is unchanged by the interchange of two rows. Since IV-4 is again of the form IV-1, the result is proved. From IV-2, the normalization constant in front of IV-1 is trivially found to be  $(N!)^{-1/2}$ .

The problem is now to compute from IV-1 and the definitions II-32 and II-74, the six quantities:  $F_{\uparrow\uparrow}^{(2)}$ ,  $F_{\downarrow\downarrow}^{(2)}$ ,  $F_{\uparrow\downarrow}^{(2)}$ ,  $F_{\downarrow\uparrow}^{(2)}$ ,  $F_{\uparrow}^{(1)}$  and  $F_{\downarrow}^{(1)}$ . Introducing the definitions

$${}_i f_j^{(k)} \equiv {}_i f_j(x_k, v_k) \equiv \left(\frac{m}{2\pi\hbar}\right)^3 u_i(x_k) \int d^3x' u_j^*(x') e^{i\frac{m}{\hbar} v_k \cdot (x' - x_k)} \quad (\text{IV-5})$$

$${}_i g_j^{(k)} \equiv {}_i g_j(x_k, v_k) \equiv \left(\frac{m}{2\pi\hbar}\right)^3 w_i(x_k) \int d^3x' w_j^*(x') e^{i\frac{m}{\hbar} v_k \cdot (x' - x_k)}$$

and noting that by virtue of IV-2,

$$\int d^3x d^3v {}_i f_j(x, v) = \int d^3x d^3v {}_i g_j(x, v) = \delta_{ij} \quad (\text{IV-6})$$

we find by direct computation that

$$F_{\uparrow\uparrow}^{(2)}(x_1, x_2; v_1, v_2) = \frac{1}{(N)(N-1)} \sum_{i=1}^m \sum_{j>i}^m \left[ {}_i f_i^{(1)} {}_j f_j^{(2)} + {}_j f_j^{(1)} {}_i f_i^{(2)} - {}_j f_i^{(1)} {}_i f_j^{(2)} - {}_i f_j^{(1)} {}_j f_i^{(2)} \right] \quad (\text{IV-7})$$

$$F_{\downarrow\downarrow}^{(2)}(x_1, x_2; v_1, v_2) = \frac{1}{(N)(N-1)} \sum_{i=1}^p \sum_{j>i}^p \left[ {}_i g_i^{(1)} {}_j g_j^{(2)} + {}_j g_j^{(1)} {}_i g_i^{(2)} - {}_j g_i^{(1)} {}_i g_j^{(2)} - {}_i g_j^{(1)} {}_j g_i^{(2)} \right] \quad (\text{IV-8})$$

$$F_{\uparrow\downarrow}^{(2)}(x_1, x_2; v_1, v_2) = \frac{1}{(N)(N-1)} \sum_{i=1}^m \sum_{j=1}^p {}_i f_i^{(1)} {}_j g_j^{(2)} \quad (\text{IV-9})$$



and

$$F_{\downarrow\uparrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{1}{N(N-1)} \sum_{i=1}^m \sum_{j=1}^p i g_i^{(1)} f_j^{(2)} \quad (\text{IV-10})$$

Integrating over  $(\underline{x}_2, \underline{v}_2)$  and summing over the second spin index gives

$$F_{\uparrow}^{(1)}(\underline{x}, \underline{v}) = \frac{1}{N} \sum_{i=1}^m i f_i(\underline{x}, \underline{v}) \quad (\text{IV-11})$$

and

$$F_{\downarrow}^{(1)}(\underline{x}, \underline{v}) = \frac{1}{N} \sum_{i=1}^p i g_i(\underline{x}, \underline{v}) \quad (\text{IV-12})$$

Direct multiplication of IV-11 and IV-12 and comparison with IV-9 and IV-10 leads to the first two desired relations

$$F_{\uparrow\downarrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{N}{N-1} F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) F_{\downarrow}^{(1)}(\underline{x}_2, \underline{v}_2) \quad (\text{IV-13})$$

and

$$F_{\downarrow\uparrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{N}{N-1} F_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1) F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_2) \quad (\text{IV-14})$$

Next, we note from IV-11 that

$$F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_2) = \frac{1}{N^2} \left[ \sum_{i=1}^m \sum_{j>i}^m \left( i f_i^{(1)} f_j^{(1)} + j f_j^{(1)} f_i^{(1)} \right) + \sum_{i=1}^m i f_i^{(1)} f_i^{(1)} \right] \quad (\text{IV-15})$$

Now, it is trivially shown from the definition IV-5 that

$$e^{-i \frac{m}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} i f_j(\underline{x}_1, \underline{v}_2) f_k(\underline{x}_2, \underline{v}_1) = i f_k(\underline{x}_1, \underline{v}_1) f_j(\underline{x}_2, \underline{v}_2) \quad (\text{IV-16})$$

Hence,

$$e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2) F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1) = \frac{1}{N^2} \left[ \sum_{i=1}^m \sum_{j>i}^m (f_{ij}^{(1)} f_{ji}^{(2)} + f_{ji}^{(1)} f_{ij}^{(2)}) + \sum_{i=1}^m f_{ii}^{(1)} f_{ii}^{(2)} \right] \quad (\text{IV-17})$$

Subtracting IV-17 from IV-15 and comparing with IV-7 leads to the desired result

$$F_{\uparrow\uparrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{N}{N-1} \left[ F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_2) - e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \times F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2) F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1) \right] \quad (\text{IV-18})$$

Similarly,

$$F_{\downarrow\downarrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{N}{N-1} \left[ F_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1) F_{\downarrow}^{(1)}(\underline{x}_2, \underline{v}_2) - e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \times F_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_2) F_{\downarrow}^{(1)}(\underline{x}_2, \underline{v}_1) \right] \quad (\text{IV-19})$$

We have proved, therefore, that for a pure state, the ansatz II-83 is equivalent to the assumption that the N particle wave function is a single Slater determinant. In a similar fashion one can readily demonstrate that II-84 also follows from this assumption.

The fact that the normalization constant in the preceding equations is  $(N/N-1)$  rather than unity has a rather interesting consequence which we now examine. Adding equations IV-13 and IV-18 and integrating over  $(\underline{x}_2, \underline{v}_2)$

gives

$$\begin{aligned}
 F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) &\equiv \int d^3x_2 d^3v_2 \left( F_{\uparrow\uparrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) + F_{\uparrow\downarrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right) \\
 &= \frac{N}{N-1} \left[ F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) - \int d^3x_2 d^3v_2 e^{-\frac{i\mathbf{m}}{\hbar}(\underline{x}_1 - \underline{x}_2) \cdot (\underline{v}_1 - \underline{v}_2)} F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1) F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2) \right]
 \end{aligned} \tag{IV-20}$$

where use has been made of the normalization condition

$$\int F^{(1)}(\underline{x}_2, \underline{v}_2) d^3x_2 d^3v_2 \equiv \left[ F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_2) + F_{\downarrow}^{(1)}(\underline{x}_2, \underline{v}_2) \right] d^3x_2 d^3v_2 = 1 \tag{IV-21}$$

Solving IV-20 leads to

$$F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) = N \int d^3x_2 d^3v_2 e^{-\frac{i\mathbf{m}}{\hbar}(\underline{x}_1 - \underline{x}_2) \cdot (\underline{v}_1 - \underline{v}_2)} F_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1) F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2) \tag{IV-22}$$

After a little algebra, this result can be rewritten in terms of the operator II-53 as follows:

$$\begin{aligned}
 F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) &= \frac{(2\pi\hbar)^3}{m^3} N \left[ \exp\left[-\frac{i\hbar}{m} \underline{\nabla}_{\underline{x}_1} \cdot \underline{\nabla}_{\underline{v}_1}\right] \left( F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) \right) \left( F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) \right) \right] \\
 &\equiv \frac{(2\pi\hbar)^3}{m^3} N \left[ \left( F_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1) \right)^2 - \frac{i\hbar}{m} \underline{\nabla}_{\underline{x}_1} F_{\uparrow}^{(1)} \cdot \underline{\nabla}_{\underline{v}_1} F_{\uparrow}^{(1)} + \dots \right]
 \end{aligned} \tag{IV-23}$$

It should be emphasized that IV-23 (and an analogous relation for  $F_{\downarrow}^{(1)}$ ) follows as a direct consequence of the form of the wave function IV-1 and involves no other assumptions or approximations. The physical content of this equation is best explored in the case of a spatially homogeneous system where the gradient terms vanish. Solving IV-23 in this case gives

$$\overline{F}_{\uparrow}^{(1)} = 0 \quad \text{or} \quad \frac{m^3}{N(2\pi\hbar)^3} \tag{IV-24}$$



which is the familiar result that for each spin species, a cell in phase space of volume  $h^3$  has occupation number 0 or 1. The state of lowest kinetic energy consistent with IV-24 and the normalization

$$N \int F_{\uparrow}^{(1)} d^3v = n_{\uparrow} \quad (\text{IV-25})$$

(where  $n_{\uparrow}$  is the number density of spin up particles) is obviously the Fermi sphere

$$F_{\uparrow}^{(1)} = \begin{cases} \frac{m^3}{N(2\pi\hbar)^3} & v \leq v_{f\uparrow} \\ 0 & v > v_{f\uparrow} \end{cases} \quad (\text{IV-26})$$

where

$$v_{f\uparrow} \equiv \left(\frac{3}{4\pi}\right)^{1/3} \left(\frac{2\pi\hbar}{m}\right) n_{\uparrow}^{1/3} \quad (\text{IV-27})$$

Thus, we conclude that IV-23 is just the exclusion principle written in q.m.d.f. language for a general pure state described by a wave function of the form IV-1. Further consequences of the  $N/N-1$  factor will be discussed in Chapter V.

Turning now to the Bose case of spinless particles, the situation is somewhat more complex. The analog of IV-1 for this case is

$$\Psi^{(N)}(1, \dots, N) = \text{const} e^{\frac{iEt}{\hbar}} \sum_{P_{ij} \dots k} u_i(x_1) u_j(x_2) \dots u_k(x_N) \quad (\text{IV-28})$$

where the sum is over the  $N!$  permutations of the single particle wave functions  $u_1 \dots u_N$  among the  $N$  particles. The complexity occurs because the  $\{u_i\}$  in general are not required to be orthonormal; no exclusion



principle acts to prevent multiple occupation of the same state. We are therefore unable to treat the Bose pure case with the same generality as the previous discussion of Fermions. If we limit ourselves, however, to certain restricted examples of the form IV-23, some insight into the relation between (the Bose form of) II-33 and IV-23 can be obtained.

Specifically, we distinguish two limiting cases: the "nondegenerate" limit characterized by the property that the  $N$  functions  $u_i$  are distinct and orthonormal so that no two particles occupy the same state; and the "totally degenerate" limit where the  $u_i$  are identical, corresponding to the "Bose condensation" of all particles into the same state.

The nondegenerate case is quite similar to the Fermi case treated earlier, and in fact can be represented as

$$\bar{\Psi}_{N.D.}^{(N)}(1, \dots, N) = \frac{1}{\sqrt{N!}} e^{\frac{iEt}{\hbar}} \begin{vmatrix} u_1(\underline{x}_1) & \dots & u_N(\underline{x}_1) \\ \vdots & & \vdots \\ u_1(\underline{x}_N) & \dots & u_N(\underline{x}_N) \end{vmatrix}_{(+)} \quad (\text{IV-29})$$

where the so-called "permanent",  $| \cdot |_{(+)}$ , is obtained from the corresponding determinant by taking all  $N!$  terms with a positive sign. The computation of  $F^{(2)}$  is straightforward and yields

$$F_{N.D.}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{1}{N(N-1)} \sum_{i=1}^N \sum_{j>i}^N \left[ f_{ii}^{(1)} f_{jj}^{(2)} + f_{jj}^{(1)} f_{ii}^{(2)} + f_{ji}^{(1)} f_{ij}^{(2)} + f_{ij}^{(1)} f_{ji}^{(2)} \right] \quad (\text{IV-30})$$

where the  $f$ 's are defined in IV-5. Integration over  $(\underline{x}_2, \underline{v}_2)$  leads to

$$F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_1) = \frac{1}{N} \sum_{i=1}^N f_i^{(1)} \quad (IV-31)$$

From IV-31 and the theorem IV-16, we find

$$\begin{aligned} F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_2) + e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_2) = \\ \frac{1}{N^2} \left[ \sum_{i=1}^N \sum_{j>i}^N (f_i^{(1)} f_j^{(2)} + f_j^{(1)} f_i^{(2)} + f_i^{(1)} f_j^{(2)} + f_j^{(1)} f_i^{(2)}) \right. \\ \left. + 2 \sum_{i=1}^N f_i^{(1)} f_i^{(2)} \right] \end{aligned} \quad (IV-32)$$

Thus,

$$\begin{aligned} F_{N.D.}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{N}{N-1} \left[ F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_2) + e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right. \\ \left. \times F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_2) \right] - \frac{2}{N(N-1)} \sum_{i=1}^N f_i^{(1)} f_i^{(2)} \end{aligned} \quad (IV-33)$$

Since the last term is seen to be of order  $1/N$ , we are led to the result

$$\begin{aligned} \lim_{N \rightarrow \infty} F_{N.D.}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_2) \\ + e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} F_{N.D.}^{(1)}(\underline{x}_2, \underline{v}_1) F_{N.D.}^{(1)}(\underline{x}_1, \underline{v}_2) \end{aligned} \quad (IV-34)$$

It is not difficult to show that if we had permitted a slight deviation from nondegeneracy by allowing  $m$  of the  $u_i$  to be identical, with  $m \ll N$  then to IV-33 would be added terms of order  $m/N$ . Since the result IV-34 is unaltered in this case, we are led to the conclusion that the Bose form of II-83 correctly describes a pure state characterized by IV-28 in the limit of large  $N$  if most of the particles are in distinctly different states.

Let us now explore the opposite extreme of complete or near-complete degeneracy. At complete degeneracy, all particles are described by the same wave function so that

$$\Psi_{c.d.}^{(N)}(1, \dots, N) = e^{\frac{iEt}{\hbar}} u_1(x_1) u_1(x_2) \dots u_1(x_N) \quad (IV-35)$$

Consequently,

$$F_{c.d.}^{(2)}(x_1, x_2; v_1, v_2) = f_1^{(1)} f_1^{(2)} \quad (IV-36)$$

and

$$F_{c.d.}^{(1)}(x_1, v_1) = f_1^{(1)} \quad (IV-37)$$

Thus

$$F_{c.d.}^{(2)}(x_1, x_2; v_1, v_2) = F_{c.d.}^{(1)}(x_1, v_1) F_{c.d.}^{(1)}(x_2, v_2) \quad (IV-38)$$

which can also be written as

$$F_{c.d.}^{(2)}(x_1, x_2; v_1, v_2) = \frac{1}{2} \left[ F_{c.d.}^{(1)}(x_1, v_1) F_{c.d.}^{(1)}(x_2, v_2) + e^{-\frac{i m}{\hbar} (x_1 - x_2) \cdot (v_1 - v_2)} F_{c.d.}^{(1)}(x_1, v_2) F_{c.d.}^{(1)}(x_2, v_1) \right] \quad (IV-39)$$



Now consider a slight departure from complete degeneracy such that one particle is in a state specified by a wave function,  $u_a$ , orthogonal to  $u_1$ . In this case (distinguished from complete degeneracy by the subscript "D")

$$\Psi_D^{(N)}(1, \dots, N) = \frac{1}{\sqrt{N}} e^{\frac{iEt}{\hbar}} \left[ u_2(x_1) u_1(x_2) \dots u_1(x_N) + u_1(x_1) u_2(x_2) \dots u_1(x_N) \right. \\ \left. + \dots + u_1(x_1) u_1(x_2) \dots u_2(x_N) \right] \quad (\text{IV-40})$$

Then

$$F_D^{(2)}(x_1, x_2; v_1, v_2) = \frac{1}{N} \left[ (N-2) f_1^{(1)} f_1^{(2)} + {}_2f_2^{(1)} f_1^{(2)} + f_1^{(1)} {}_2f_2^{(2)} \right. \\ \left. + {}_2f_1^{(1)} f_2^{(2)} + f_2^{(1)} {}_2f_1^{(2)} \right] \quad (\text{IV-41})$$

and

$$F_D^{(1)}(x_1, v_1) = \frac{N-1}{N} f_1^{(1)} + \frac{1}{N} {}_2f_2^{(1)} \quad (\text{IV-42})$$

From IV-42 we find

$$F_D^{(1)}(x_1, v_1) F_D^{(1)}(x_2, v_2) + e^{-\frac{i m}{\hbar} (v_1 - v_2) \cdot (x_1 - x_2)} F_D^{(1)}(x_2, v_1) F_D^{(1)}(x_1, v_2) \\ = 2 \left( \frac{N-1}{N} \right)^2 f_1^{(1)} f_1^{(2)} + \frac{2}{N^2} {}_2f_2^{(1)} {}_2f_2^{(2)} + \frac{N-1}{N^2} \left[ f_1^{(1)} {}_2f_2^{(2)} \right. \\ \left. + {}_2f_2^{(1)} f_1^{(2)} + f_2^{(1)} {}_2f_1^{(2)} + {}_2f_1^{(1)} f_2^{(2)} \right] \quad (\text{IV-43})$$



Using IV-41 and IV-36, we have finally

$$F_D^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) + \frac{N-1}{N} F_{c.d.}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = F_D^{(1)}(\underline{x}_1, \underline{v}_1) F_D^{(1)}(\underline{x}_2, \underline{v}_2) \\ + e^{-\frac{i m}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} F_D^{(1)}(\underline{x}_2, \underline{v}_1) F_D^{(1)}(\underline{x}_1, \underline{v}_2) + \left( \text{terms of order } \frac{1}{N^2} \right) \quad (\text{IV-44})$$

Thus, it is seen that a completely degenerate Bose pure state of the form IV-35 is properly described by the Hartree approximation (or, equivalently though unnecessarily, by the Hartree-Fock ansatz II-83 with  $C = 1/2$ ) while slight deviations from this state are not in general subsumed under II-83, the proper (pure state) modification in the latter case being

$$\lim_{N \rightarrow \infty} F^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \left( F^{(1)}(\underline{x}_1, \underline{v}_1) F^{(1)}(\underline{x}_2, \underline{v}_2) + e^{-\frac{i m}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right. \\ \left. \times F^{(1)}(\underline{x}_2, \underline{v}_1) F^{(1)}(\underline{x}_1, \underline{v}_2) \right) - F_{c.d.}^{(1)}(\underline{x}_1, \underline{v}_1) F_{c.d.}^{(1)}(\underline{x}_2, \underline{v}_2) \quad (\text{IV-45})$$

The foregoing results have a certain bearing on the types of physical situations where II-83 et seq. constitute a viable approximation to the mixed case (i.e. statistical mechanics). Recall that the "normalization" constant,  $C$ , appearing in II-83 has not yet been specified. Clearly, however, it must be close to unity if dynamical exchange effects (i.e. those corrections to the particle interactions occasioned by the requisite symmetry properties) are to be treatable as relatively small corrections to the Hartree approximation. For nondegenerate systems (in the statistical sense), where particles behave in an essentially classical fashion, exchange

effects are negligible and  $C$  assumes its classical value of unity. At low temperatures, however,  $C$  must approach the value appropriate to the (pure) ground state, since the pure and mixed cases merge at zero temperature. Appreciable variation from unity of this value is, therefore, indicative of a breakdown in the applicability of the approximation scheme. For the Fermi case, we have shown that no such difficulty arises in the Hartree-Fock approximation, and that the appropriate value for  $C$  is  $N/N-1$  for degenerate systems, and (of course) unity for nondegenerate systems -- a negligible distinction in the limit of large  $N$ . With Bosons, however, the limiting pure case value of  $C = 1/2$  indicates that a single ansatz of the form II-83 (and, subsequently, II-84 and II-85) cannot be expected to adequately represent a Bose system over the whole range of temperature.\* Indeed, we have shown that at zero temperature, the Hartree and Hartree-Fock approximations are equivalent so that one can bypass the second stage of approximation entirely in this limit. The implication\*, therefore, is that the proper forms of II-83 et seq. must undergo a discontinuous change at the temperature of Bose-Einstein condensation, and that these equations, if not so modified, can only be applied to systems appreciably above this temperature. In view of this circumstance, low temperature Bose systems lie beyond the proper scope of the present work, although there are indications (e.g. IV-45) the formalism need not be radically altered to include them as well. We therefore will sacrifice some of the generality maintained to this point by limiting our subsequent considerations to spin  $1/2$  systems.

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\*That some modification of the formalism should be required at very low temperatures is, of course, a reflection of the radical changes which occur below the temperature of Bose-Einstein condensation -- a phenomenon which in a sense has been anticipated by the assumption that the ground state in the absence of correlation is described by IV-35.

### B. Second Quantum Vlasov Equation

Proceeding analogously to Section III-B, we introduce II-83 into II-76 (with  $R=1$ ). Since our main concern will be with degenerate Fermi systems, the constant  $C$  in II-83 is taken to be  $N/N-1$  as discussed previously. The resulting equations for the "spin up" and "spin Down"  $\tilde{F}^{(1)}_S$  are

$$\begin{aligned} \frac{\partial \tilde{F}^{(1)}_{\uparrow}}{\partial t} + \left\{ \tilde{F}^{(1)}_{\uparrow}, H^{(1)}(\underline{x}_1, \underline{v}_1; t) \right\}_{\text{G.P.B.}}^{(1)} &= \frac{i}{\hbar} \left[ \exp \left[ -\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1} \right] - 1 \right] \\ &\times \left( N g^2 \int d^3 \underline{x}_2 d^3 \underline{v}_2 \left( \tilde{F}^{(1)}_{\uparrow}(\underline{x}_2, \underline{v}_2, t) + \tilde{F}^{(1)}_{\downarrow}(\underline{x}_2, \underline{v}_2, t) \right) \phi(\underline{x}_1 - \underline{x}_2) \right) \tilde{F}^{(1)}_{\uparrow}(\underline{x}_1, \underline{v}_1, t) \\ &- \frac{i}{\hbar} N g^2 \int d^3 \underline{x}_2 d^3 \underline{v}_2 \left[ \exp \left[ -\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1} \right] - 1 \right] \left( \phi(\underline{x}_1 - \underline{x}_2) \right) \\ &\times \left( e^{-\frac{i m}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}_{\uparrow}(\underline{x}_1, \underline{v}_2, t) \tilde{F}^{(1)}_{\uparrow}(\underline{x}_2, \underline{v}_1, t) \right) \end{aligned} \quad (\text{IV-46})$$

and an identical equation obtained from the above by the substitution  $\tilde{F}^{(1)}_{\uparrow} \leftrightarrow \tilde{F}^{(1)}_{\downarrow}$ . Comparison with III-9 shows that aside from factors of  $N/N-1$ , the departure from the Hartree approximation is contained in the last term on the r.h.s. of IV-46 which represents the so-called "exchange interaction" between particles of parallel spin. This term can be considerably simplified by means of the identity

$$\begin{aligned} &\int d^3 \underline{x}_2 d^3 \underline{v}_2 \left[ \exp \left[ -\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1} \right] - 1 \right] \left( \phi(\underline{x}_1 - \underline{x}_2) \right) \left( A(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right) \\ &\equiv \frac{1}{(2\pi)^3} \int d^3 \underline{x}_2 d^3 \underline{v}_2 d^3 \underline{q} e^{i \underline{q} \cdot (\underline{x}_1 - \underline{x}_2)} f(\underline{q}) \left[ A(\underline{x}_1, \underline{x}_2; \underline{v}_1 + \frac{\hbar}{m} \underline{q}, \underline{v}_2) \right. \\ &\quad \left. - A(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right] \end{aligned} \quad (\text{IV-47})$$



where  $f(\underline{q})$ , the Fourier transform of the interaction potential,  $\phi$ , is defined in II-78. Then,

$$\begin{aligned} & -Ng^2 \frac{i}{\hbar} \int d^3x_2 d^3v_2 \left[ \exp\left[-\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1}\right] - 1 \right] \left( \phi(\underline{x}_1 - \underline{x}_2) \right) \left( e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right. \\ & \times \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1, t) \Big) = -\frac{Ng^2}{(2\pi)^3} \frac{i}{\hbar} \int d^3x_2 d^3v_2 d^3q f(\underline{q}) \\ & \times \left[ e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) \right. \\ & \left. - e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2 - \frac{\hbar}{m} \underline{q}) \cdot (\underline{x}_1 - \underline{x}_2)} \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1, t) \right] \end{aligned}$$

(IV-48)

Now, by means of a change in variable and a Maclaurin expansion, one finds

$$\begin{aligned} & \int d^3x_2 d^3v_2 d^3q f(\underline{q}) e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) \\ & = \frac{\hbar^3}{m^3} \left[ \exp\left[-\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1}\right] \right] \left( \int d^3x_2 d^3q' d^3q e^{i\underline{q}' \cdot (\underline{x}_1 - \underline{x}_2)} f(\underline{q}) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) \right) \\ & \times \left( \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right) \end{aligned}$$

(IV-49)

Performing the  $\underline{q}'$  and  $\underline{x}_2$  integrations reduces this to

$$(2\pi)^3 \left[ \exp\left[-\frac{i\hbar}{m} \nabla_{\underline{x}_1} \cdot \nabla_{\underline{v}_1}\right] \right] \left( \int d^3v' f\left(\frac{m}{\hbar} (\underline{v}' - \underline{v}_1)\right) \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}', t) \right) \left( \widetilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right)$$

(IV-50)



Similarly,

$$\begin{aligned}
 & \int d^3x_2 d^3v_2 d^3q f(q) e^{-i\frac{m}{\hbar}(v_1 - v_2 - \frac{\hbar}{m}q) \cdot (x_1 - x_2)} \widetilde{F}_{\uparrow}^{(1)}(x_1, v_2, t) \widetilde{F}_{\uparrow}^{(1)}(x_2, v_1, t) \\
 &= \frac{\hbar^3}{m^3} \left[ \exp \left[ -i\frac{\hbar}{m} \nabla_{x_1} \cdot \nabla_{v_1} \right] \right] \left( \widetilde{F}_{\uparrow}^{(1)}(x_1, v_1, t) \right) \left( \int d^3y d^3v_2 d^3q f(q) e^{i y \cdot (v_1 - v_2 - \frac{\hbar}{m}q)} \right. \\
 & \quad \left. \times \widetilde{F}_{\uparrow}^{(1)}(x_1, v_2, t) \right)
 \end{aligned}
 \tag{IV-51}$$

which in turn becomes

$$(2\pi)^3 \left[ \exp \left[ -i\frac{\hbar}{m} \nabla_{x_1} \cdot \nabla_{v_1} \right] \right] \left( \widetilde{F}_{\uparrow}^{(1)}(x_1, v_1, t) \right) \left( \int d^3v' f\left(\frac{m}{\hbar}(v' - v_1)\right) \widetilde{F}_{\uparrow}^{(1)}(x_1, v', t) \right)
 \tag{IV-52}$$

Thus, if we define the exchange potential,  $\phi_{\uparrow}^{\text{exch}}(x_1, v_1, t)$ , as

$$\phi_{\uparrow}^{\text{exch}}(x_1, v_1, t) \equiv -N \int d^3v' f\left(\frac{m}{\hbar}(v' - v_1)\right) \widetilde{F}_{\uparrow}^{(1)}(x_1, v', t)
 \tag{IV-53}$$

and the self consistent field

$$\phi^{\text{scF}}(x_1, t) \equiv N \int d^3x_2 d^3v_2 \left( \widetilde{F}_{\uparrow}^{(1)}(x_2, v_2, t) + \widetilde{F}_{\downarrow}^{(1)}(x_2, v_2, t) \right) \phi(x_1 - x_2)
 \tag{IV-54}$$

we see from the foregoing and the definition (II-56) of the Generalized Poisson Bracket, that IV-46 becomes simply

$$\frac{\partial \widetilde{F}_{\uparrow}^{(1)}}{\partial t} + \left\{ \widetilde{F}_{\uparrow}^{(1)}(x_1, v_1, t), H_{\uparrow}^{(1)}(x_1, v_1, t) \right\}_{\text{G.P.B.}}^{(1)} = 0
 \tag{IV-55}$$

where the Hartree-Fock Hamiltonian,  $H_{\uparrow}^{(1)}$ , is given by

$$H_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \equiv \frac{1}{2} m v_1^2 + g^2 \phi^{\text{ext}}(\underline{x}_1, t) + g^2 \phi^{\text{scf}}(\underline{x}_1, t) + g^2 \phi_{\uparrow}^{\text{exch}}(\underline{x}_1, \underline{v}_1, t) \quad (\text{IV-56})$$

Equation IV-55 and the precisely similar result for  $\tilde{F}_{\downarrow}^{(1)}$ :

$$\frac{\partial \tilde{F}_{\downarrow}^{(1)}}{\partial t} + \left\{ \tilde{F}_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1, t), H_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right\}_{\text{GPB}}^{(1)} = 0 \quad (\text{IV-57})$$

are the desired forms of the second quantum Vlasov equation. We observe that the spin "up" and "down" subsystems are coupled only through the self-consistent field and, of course, the normalization condition

$$\int d^3x, d^3v, \left( \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) + \tilde{F}_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right) = 1 \quad (\text{IV-58})$$

Since, however, the  $\underline{z}$  component of total spin,  $\sum_z$ , is a conserved quantity, the two  $\tilde{F}^{(1)}$ 's obey in fact independent normalizations

$$\int d^3x, d^3v, \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) = a \quad (\text{IV-59})$$

$$\int d^3x, d^3v, \tilde{F}_{\downarrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) = b \quad (\text{IV-60})$$

where

$$a + b = 1 \quad (\text{IV-61})$$

$$\frac{N}{2} (a - b) = \sum_z \quad (\text{IV-62})$$

Of particular interest in many situations is the special case\* where  $a = b = 1/2$  and, more restrictedly,

$$\tilde{F}_{\uparrow}^{(1)} = \tilde{F}_{\downarrow}^{(1)} \equiv \frac{1}{2} \tilde{F}_{\text{NORM}}^{(1)} \quad (\text{IV-63})$$

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\*See footnote page 70.

For this so-called "normal" system where both spin species behave identically, a single quantum Vlasov equation replaces IV-55 and IV-57:

$$\frac{\partial \tilde{F}_{\text{NORM}}^{(1)}}{\partial t} + \left\{ \tilde{F}_{\text{NORM}}^{(1)}(\underline{x}_1, \underline{v}_1, t), H_{\text{NORM}}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right\}_{\text{G.P.B.}}^{(1)} \equiv 0 \quad (\text{IV-64})$$

where

$$H_{\text{NORM}}^{(1)}(\underline{x}_1, \underline{v}_1, t) = \frac{1}{2} m v_1^2 + g^2 \phi^{\text{ext}}(\underline{x}_1, t) + g^2 \phi^{\text{scF}}(\underline{x}_1, t) + g^2 \phi_{\text{NORM}}^{\text{exch}}(\underline{x}_1, \underline{v}_1, t) \quad (\text{IV-65})$$

and

$$\phi_{\text{NORM}}^{\text{exch}}(\underline{x}_1, \underline{v}_1, t) = -\frac{N}{2} \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v}' - \underline{v}_1)\right) \tilde{F}_{\text{NORM}}^{(1)}(\underline{x}_1, \underline{v}', t) \quad (\text{IV-66})$$

Various equivalent forms of IV-55, IV-57 and IV-64 are often a more convenient starting point than these compact equations. We list them here for future reference:

$$\begin{aligned} \frac{\partial \tilde{F}_{\uparrow}^{(1)}}{\partial t} + \underline{v}_1 \cdot \nabla_{\underline{x}_1} \tilde{F}_{\uparrow}^{(1)} - \frac{1}{m} \nabla_{\underline{x}_1} g^2 (\phi^{\text{ext}} + \phi^{\text{scF}}) \cdot \nabla_{\underline{v}_1} \tilde{F}_{\uparrow}^{(1)} = \\ \frac{i\hbar}{2m} \nabla_{\underline{x}_1}^2 \tilde{F}_{\uparrow}^{(1)} + \frac{ig^2}{\hbar} \sum_{n=2}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \frac{\partial^n (\phi^{\text{ext}} + \phi^{\text{scF}})}{\partial x_1^k \partial x_1^l \dots} \frac{\partial^n \tilde{F}_{\uparrow}^{(1)}}{\partial v_1^k \partial v_1^l \dots} \\ + \frac{ig^2}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n \left[ \frac{\partial^n \phi_{\uparrow}^{\text{exch}}}{\partial x_1^k \partial x_1^l \dots} \frac{\partial^n \tilde{F}_{\uparrow}^{(1)}}{\partial v_1^k \partial v_1^l \dots} - \frac{\partial^n \phi_{\uparrow}^{\text{exch}}}{\partial v_1^k \partial v_1^l \dots} \frac{\partial^n \tilde{F}_{\uparrow}^{(1)}}{\partial x_1^k \partial x_1^l \dots} \right] \end{aligned}$$

(IV-67)



and

$$\begin{aligned} \frac{\partial \tilde{F}_{\uparrow}^{(1)}}{\partial t} + \underline{v}_1 \cdot \nabla_{\underline{x}_1} \tilde{F}_{\uparrow}^{(1)} - \frac{i\hbar}{2m} \nabla_{\underline{x}_1}^2 \tilde{F}_{\uparrow}^{(1)} - \frac{ig^2}{\hbar(2\pi)^3} \int d^3 \underline{q} e^{i\underline{q} \cdot \underline{x}_1} \\ \times \left( f^{\text{ext}}(\underline{q}, t) + f^{\text{scF}}(\underline{q}, t) \right) \left[ \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) - \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_1, t) \right] \\ + \frac{ig^2 N}{(2\pi)^3 \hbar} \int d^3 \underline{x}_2 d^3 \underline{v}_2 d^3 \underline{q} f(\underline{q}) \left[ e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \tilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) \right. \\ \left. - e^{-\frac{im}{\hbar} (\underline{v}_1 - \underline{v}_2 - \frac{\hbar}{m} \underline{q}) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}_{\uparrow}^{(1)}(\underline{x}_1, \underline{v}_2, t) \tilde{F}_{\uparrow}^{(1)}(\underline{x}_2, \underline{v}_1, t) \right] = 0 \end{aligned}$$

(IV-68)

where the  $f$ 's are defined in III-17, III-18 and II-78. The corresponding equations for  $\tilde{F}_{\downarrow}^{(1)}$  and  $\tilde{F}_{\text{NORM}}^{(1)}$  are trivially obtained from the above.

The discussion of Section III-B can now be taken over in toto and applied to the significance and utility of the second quantum Vlasov equation. Since such repetition is of little value, we shall proceed directly to illustrative applications of this equation. In Section C, the spatially homogeneous system considered in III-C will be re-examined in detail. Of particular interest is the appearance of a new mode of excitation, the spin wave, which is brought about by the exchange potential much in the same fashion as "plasma oscillations" are sustained by the self-consistent field. In Section D, we reconsider the macroscopic equations of quantum hydrodynamic transport and obtain additional terms arising from the exchange interaction.



An especially powerful application of the second quantum Vlasov equation will be given in Chapter V, where the formal equivalence of the time-independent form of IV-64 and the Schroedinger equation for a stationary pure state of the form IV-1 is exploited to study the ground state of spatially inhomogeneous many-Fermion systems -- the many-electron atom in particular. Furthermore, the fact that the very same IV-64 applies to systems at non-zero temperature, leads readily to the thermodynamic properties of such systems.

### C. Spatially Homogeneous Systems

We consider the problem formulated in III-C, specialized to the case of spin 1/2 particles. For  $t < 0$ , both spin subsystems are assumed to be spatially uniform and in thermal equilibrium at temperature  $T$ . We permit, however, an unequal population of spin states as described by IV-59 through IV-62, which in the present case take the form (cf. III-24)

$$N \int \tilde{F}_{\uparrow}^{(n)}(\underline{v}, t < 0) d^3v = a n \equiv n_{\uparrow} \quad (\text{IV-69})$$

and

$$N \int \tilde{F}_{\downarrow}^{(n)}(\underline{v}, t < 0) d^3v = (1-a) n \equiv n_{\downarrow} \quad (\text{IV-70})$$

The first problem, therefore, is to obtain a description of the consequent equilibrium situation.

Since the self-consistent field is spatially constant, the two spin subsystems decouple and may be treated independently. Concentrating on  $\tilde{F}_{\uparrow}^{(n)}$ , the second quantum Vlasov equation (IV-55) again reduces to an

equation of the form III-22, a time independent solution to which is provided by any spatially independent  $\tilde{F}_{\uparrow}^{(n)}$ . Instead of introducing a microcanonical ensemble and going through the somewhat cumbersome machinery of ensemble theory to determine  $\tilde{F}_{\uparrow}^{(n)}$ , we appeal to the quantum mechanical H-theorem which, for the present problem, states that in thermal equilibrium, the entropy is extremal viz.

$$\delta \int d^3v \left[ \left( \frac{N h^3}{m^3} \tilde{F}_{\uparrow}^{(n)} \right) \log \left( \frac{N h^3}{m^3} \tilde{F}_{\uparrow}^{(n)} \right) + \left( 1 - \frac{N h^3}{m^3} \tilde{F}_{\uparrow}^{(n)} \right) \log \left( 1 - \frac{N h^3}{m^3} \tilde{F}_{\uparrow}^{(n)} \right) \right] = 0 \quad (\text{IV-71})$$

where the symbol  $\delta$  stands for an arbitrary variation of  $\tilde{F}_{\uparrow}^{(n)}$ , subject, however, to IV-69 and the additional constraint

$$\delta \int d^3v \epsilon_{\uparrow}(\tilde{F}_{\uparrow}^{(n)}) = 0 \quad (\text{IV-72})$$

where  $\epsilon_{\uparrow}$  is the total energy density expressed as a functional of  $\tilde{F}_{\uparrow}^{(n)}$ .

As this quantity has not yet been derived, we take this opportunity to do so.

In general, the (ensemble averaged) expectation value of the total energy is obtained from II-63 and II-60, written in terms of  $\tilde{F}^{(N)}$ . Specifically, we find for the combined energy of both spin subsystems the general expression

$$\begin{aligned} E = & \text{Re} \left\{ N \int d^3x, d^3v, \frac{1}{2} m v^2 \left( \sum_{\alpha_1=-S}^{+S} \tilde{F}_{\alpha_1}^{(n)}(\underline{x}_1, \underline{v}_1, t) \right) \right. \\ & + \frac{N(N-1)}{2} \int d^3x, d^3v, d^3x_2, d^3v_2, g^2 \phi(\underline{x}_1 - \underline{x}_2) \left( \sum_{\alpha_1, \alpha_2=-S}^{+S} \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2; t) \right) \\ & \left. + N \int d^3x, d^3v, g^2 \phi^{\text{ext}}(\underline{x}_1, t) \left( \sum_{\alpha_1=-S}^{+S} \tilde{F}_{\alpha_1}^{(n)}(\underline{x}_1, \underline{v}_1, t) \right) \right\} \end{aligned}$$

(IV-73)

which, in the Hartree-Fock approximation, becomes

$$\begin{aligned}
 E_{H.F.} = & \text{Re} \int d^3x, d^3v, \left(\frac{1}{2} m v^2\right) \left( \widetilde{F}_{\uparrow}^{(0)}(x, v, t) + \widetilde{F}_{\downarrow}^{(0)}(x, v, t) \right) \\
 & + \int d^3x, \langle n_{\uparrow}(x, t) + n_{\downarrow}(x, t) \rangle \left( g^2 \phi^{\text{ext}}(x, t) + \frac{1}{2} g^2 \phi^{\text{scF}}(x, t) \right) \\
 & - \text{Re} \frac{N^2}{2} g^2 \int d^3x_1, d^3x_2, d^3v_1, d^3v_2 \phi(x_1 - x_2) e^{-\frac{i m}{\hbar} (v_1 - v_2) \cdot (x_1 - x_2)} \\
 & \times \left[ \widetilde{F}_{\uparrow}^{(0)}(x_1, v_1, t) \widetilde{F}_{\uparrow}^{(0)}(x_2, v_2, t) + \widetilde{F}_{\downarrow}^{(0)}(x_1, v_1, t) \widetilde{F}_{\downarrow}^{(0)}(x_2, v_2, t) \right]
 \end{aligned}
 \tag{IV-74}$$

In the present example, IV-74 leads to the desired result for the energy density:

$$\begin{aligned}
 \epsilon_{\uparrow} = & \int d^3v, \left(\frac{1}{2} m v^2\right) \left( N \widetilde{F}_{\uparrow}^{(0)}(v) \right) - \frac{g^2}{2} \int d^3v_1, d^3v_2 f\left(\frac{m}{\hbar} (v_1 - v_2)\right) \\
 & \times \left( N \widetilde{F}_{\uparrow}^{(0)}(v_1) \right) \left( N \widetilde{F}_{\uparrow}^{(0)}(v_2) \right)
 \end{aligned}
 \tag{IV-75}$$

Returning to IV-71, we perform the indicated variation, using the method of Lagrange multipliers to include the constraints IV-69 and IV-72. The result is the integral equation\*

$$\widetilde{F}_{\uparrow}^{(0)}(v) = \frac{m^3}{N \hbar^3} \left[ \exp \left( \frac{\frac{1}{2} m v^2 - g^2 \int d^3v' f\left(\frac{m}{\hbar} (v - v')\right) (N \widetilde{F}_{\uparrow}^{(0)}(v')) - \mu_{\uparrow}}{\hbar T} \right) + 1 \right]^{-1} \tag{IV-76}$$

where the Lagrange multipliers have been identified with the temperature and chemical potential,  $\mu_{\uparrow}$ , in the usual fashion. The latter quantity is determined by IV-69. Note that in the absence of the exchange term, IV-76 reduces to the usual Fermi-Dirac distribution function.

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\*Equation IV-76 has received rather scant attention in the literature. It was first derived in 1947 by Koppe (35), and subsequently studied by Wohlfarth (36) and Lidiard (37). These investigations were limited to the case of a degenerate electron gas and were motivated by the fact that the solution to IV-76 leads to an expression for the low temperature specific heat which is significantly less than the Sommerfeld free-electron value.



Because of the complexity of IV-76, we must limit its discussion to the case of Coulomb interactions. First, we observe that at zero temperature, a solution of this equation is provided by the zero temperature Fermi-Dirac distribution, IV-26. To demonstrate this, we insert IV-26 into the r.h.s. of IV-76 with  $g^2$  and  $f$  given by III-39. The integration over  $v'$  is straightforward and we find that the r.h.s. of IV-76 becomes

$$\frac{m^3}{N h^3} \left[ \exp \left( \frac{\frac{1}{2} m v^2 - \frac{e^2 m v_{f\uparrow}}{\pi \hbar} \left[ 1 - \frac{u^2-1}{2u} \ln \left| \frac{1+u}{1-u} \right| \right] - \mu_{\uparrow}}{k T} \right) + 1 \right]^{-1} \quad (\text{IV-77})$$

where  $u \equiv v/v_{f\uparrow}$ . It is readily seen that a necessary and sufficient condition for this expression to approach IV-26 at zero temperature is that the function

$$g(u) \equiv u^2 + \left( \frac{e^2}{\hbar \pi v_{f\uparrow}} \right) \left( \frac{u^2-1}{u} \right) \ln \left| \frac{1+u}{1-u} \right| \quad (\text{IV-78})$$

be monotonically increasing for  $u \geq 0$ . Setting  $dg/du$  equal to zero leads to the equation

$$\frac{e^2}{\hbar \pi v_{f\uparrow}} = \frac{-2u^3}{(u^2+1) \ln \left| \frac{1+u}{1-u} \right| - 2u} \quad (\text{IV-79})$$

which has no solution for positive  $u$ , thereby guaranteeing the monotonicity of  $g(u)$  for all  $v_{f\uparrow}$ . Thus, we have shown that at zero temperature, the effect of exchange is merely to alter the relation between the chemical potential and the Fermi velocity (i.e. the density), the new relation being

$$\frac{1}{2} m v_{f\uparrow}^2 - \frac{e^2 m v_{f\uparrow}}{\pi \hbar} = \mu_{\uparrow} \quad (\text{IV-80})$$



At non-zero temperature, the situation is naturally more complicated. Lidiard (37), however, has shown that at very low temperatures, an approximate solution of IV-76 is provided by the Fermi-Dirac distribution appropriate to an effective temperature<sup>\*</sup>,  $\tau_f$  different from the actual temperature, T. Specifically, he finds

$$\tilde{F}_f^{(n)}(v, T) \approx \frac{m^3}{N h^3} \left[ \exp\left(\frac{\frac{1}{2} m (v^2 - v_{f\uparrow}^2(n_f, \tau_f))}{k \tau_f(T)}\right) + 1 \right]^{-1} \quad (\text{IV-81})$$

where  $\tau_f$  is related to T via the transcendental equation

$$\frac{T}{\tau_f} = 1 + \frac{e^2}{\hbar \pi v_{f\uparrow}(n_f, \tau_f=0)} \ln \left[ (1.15) \left( \frac{\frac{1}{2} m v_{f\uparrow}^2(n_f, \tau_f=0)}{k \tau_f} \right) \right] \quad (\text{IV-82})$$

and  $v_{f\uparrow}(n_f, \tau_f)$  is determined from IV-69.

Thus, IV-81, IV-82, and IV-26 in the limit of zero temperature are the desired equilibrium distributions for  $\tilde{F}_f^{(n)}$  in the Coulomb case. It should be emphasized, however, that their validity hinges on the assumption that they are unique solutions to the integral equation IV-76. Due to the complexity of this equation, such uniqueness is by no means apparent and can only be established by a more detailed analysis which lies beyond the scope of the present work.

Completing the description of the equilibrium situation, we now compute the total energy density from IV-75 and the appropriate equilibrium distribution function. The velocity space integrations, while trivial at zero temperature, are somewhat involved for  $T \neq 0$  and

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\*Equivalently, one can speak of a (temperature dependent) effective mass.

are given by Lidiard (37) and Yokota (38). The result for the average total energy per particle is

$$\frac{\epsilon}{n} \equiv \frac{\epsilon_{\uparrow} + \epsilon_{\downarrow}}{n} = \frac{3}{5} \left[ \frac{\pi^2 \hbar^2}{2m} \left( \frac{3n}{\pi} \right)^{2/3} \right] \left[ a^{2/3} \left( a^{5/3} \left( 1 + \frac{5}{12} \chi_{\uparrow}^2 \right) + (1-a)^{5/3} \left( 1 + \frac{5}{12} \chi_{\downarrow}^2 \right) \right) \right] \\ - \frac{3}{4} \left[ e^2 \left( \frac{3n}{\pi} \right)^{1/3} \right] \left[ a^{1/3} \left( a^{4/3} \left( 1 + \frac{\chi_{\uparrow}^2}{6} \ln \left( \frac{\chi_{\uparrow}}{6.20} \right) \right) + (1-a)^{4/3} \left( 1 + \frac{\chi_{\downarrow}^2}{6} \ln \left( \frac{\chi_{\downarrow}}{6.20} \right) \right) \right) \right] \quad (\text{IV-83})$$

where  $a$  is defined in IV-69 and  $\chi_{\uparrow}$  and  $\chi_{\downarrow}$  are determined from the relations

$$\frac{\pi \hbar^2 T}{(2a)^{2/3} \frac{\pi^2 \hbar^2}{2m} \left( \frac{3n}{\pi} \right)^{2/3}} \equiv \chi_{\uparrow} - \frac{e^2 m}{(2a)^{1/3} \hbar^2 \pi^2 \left( \frac{3n}{\pi} \right)^{1/3}} \chi_{\uparrow} \ln \left( \frac{\chi_{\uparrow}}{1.14} \right) \quad (\text{IV-84})$$

and

$$\frac{\pi \hbar^2 T}{(2(1-a))^{2/3} \frac{\pi^2 \hbar^2}{2m} \left( \frac{3n}{\pi} \right)^{2/3}} \equiv \chi_{\downarrow} - \frac{e^2 m}{(2(1-a))^{1/3} \hbar^2 \pi^2 \left( \frac{3n}{\pi} \right)^{1/3}} \chi_{\downarrow} \ln \left( \frac{\chi_{\downarrow}}{1.14} \right) \quad (\text{IV-85})$$

It is interesting to note from IV-83 that a critical density,  $n_c(T)$ , exists such that below this value, the  $|a| = 1$  (or "ferromagnetic") state has lower energy than the  $a = 1/2$  (or "paramagnetic") state\*.

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\*At zero temperature, it is easily shown that the energy is minimal at one of these two values.

At  $T = 0$ ,  $x_{\downarrow} = x_{\uparrow} = 0$  and we find for  $n_c$

$$n_c (T=0) = \frac{125 m^3 e^6}{24 \pi^5 (2^{1/3} + 1)^3 \hbar^6} \quad (\text{IV-86})$$

a value first derived by Bloch (39). However, as noted by Seitz (40), we expect this result to be significantly altered when correlation effects are taken into account. In any event, when we subsequently limit our considerations to  $a = 1/2$ , it is understood that the density is assumed to be sufficiently large to insure that this is indeed the state of lower energy.

Turning now to the response of the system to weak external forces, we proceed in strict analogy to III-25 et seq, the basic equation now being IV-68 instead of III-19. After a little manipulation, we find that III-33 is replaced by the pair of equations (with obvious notation)

$$\begin{aligned} & \left( -\omega + \underline{v} \cdot \underline{q} + \frac{\hbar q^2}{2m} \right) \mathcal{F}_1^{\uparrow}(\underline{q}, \underline{v}, \omega) - \frac{g^2}{\hbar} \left[ F_0^{\uparrow}(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0^{\uparrow}(\underline{v}) \right] \\ & \times \left[ f^{\text{ext}}(\underline{q}, \omega) + f(\underline{q}) \int d^3 v' \left( \mathcal{F}_1^{\uparrow}(\underline{q}, \underline{v}', \omega) + \mathcal{F}_1^{\downarrow}(\underline{q}, \underline{v}', \omega) \right) \right] \\ & - \frac{g^2}{\hbar} \left[ \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) \left( F_0^{\uparrow}(\underline{v}' + \frac{\hbar}{m} \underline{q}) - F_0^{\uparrow}(\underline{v}') \right) \right] \left[ \mathcal{F}_1^{\uparrow}(\underline{q}, \underline{v}, \omega) \right] \\ & + \frac{g^2}{\hbar} \left[ F_0^{\uparrow}(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0^{\uparrow}(\underline{v}) \right] \left[ \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) \mathcal{F}_1^{\uparrow}(\underline{q}, \underline{v}', \omega) \right] = 0 \end{aligned}$$



and a similar equation for  $\mathcal{F}_1^\downarrow$ . The physical content of these equations becomes clearer if we consider the special case,  $a = 1/2$ , and define

$$\begin{aligned} F_0^\uparrow &= F_0^\downarrow \equiv \frac{1}{2} F_0 \\ \mathcal{F}_1^+ &\equiv \mathcal{F}_1^\uparrow + \mathcal{F}_1^\downarrow \\ \mathcal{F}_1^- &\equiv \mathcal{F}_1^\uparrow - \mathcal{F}_1^\downarrow \end{aligned} \quad (\text{IV-88})$$

Then, we have

$$\begin{aligned} &(-\omega + \underline{v} \cdot \underline{q} + \frac{\hbar q^2}{2m}) \mathcal{F}_1^+ - \frac{g^2}{\hbar} \left[ F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v}) \right] \left[ f^{\text{ext}}(\underline{q}, \omega) \right. \\ &+ \left. f(\underline{q}) \int d^3 v' \mathcal{F}_1^+(\underline{q}, \underline{v}', \omega) \right] - \frac{g^2}{2\hbar} \left[ \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) (F_0(\underline{v}' + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v}')) \right] \\ &\times \mathcal{F}_1^+(\underline{q}, \underline{v}, \omega) + \frac{g^2}{2\hbar} \left[ F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v}) \right] \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) \mathcal{F}_1^+(\underline{q}, \underline{v}', \omega) = 0 \end{aligned} \quad (\text{IV-89})$$

and

$$\begin{aligned} &(-\omega + \underline{v} \cdot \underline{q} + \frac{\hbar q^2}{2m}) \mathcal{F}_1^- - \frac{g^2}{2\hbar} \left[ \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) (F_0(\underline{v}' + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v}')) \right] \\ &\times \mathcal{F}_1^- + \frac{g^2}{2\hbar} \left[ F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v}) \right] \int d^3 v' f\left(\frac{m}{\hbar}(\underline{v} - \underline{v}')\right) \mathcal{F}_1^-(\underline{q}, \underline{v}', \omega) = 0 \end{aligned} \quad (\text{IV-90})$$



The first of these equations determines the fluctuations in density caused by the external field and represents the exchange-corrected form of III-33. In the case of Coulomb interactions, it has been used by von Roos and Zmuidzinis (13) to obtain corrections to the dispersion relation, III-42, in the long wavelength ( $q \rightarrow 0$ ) limit. IV-90, on the other hand, describes a new mode of collective excitation, uncoupled from the density fluctuations, which are spin density waves and represent spatially periodic asymmetries in the relative population of the two spin states. Of particular interest are standing spin density waves ( $\omega \rightarrow 0$ ) the potential importance of which has been emphasized by Overhauser(41) for the electron gas. Indeed, he has claimed that such waves lower the system energy with respect to that of the spatially uniform state-even in the high density limit. If this is true, the spatially uniform state would be unstable with respect to the formation of standing spin density waves and the equilibrium distribution function, IV-81, would have to be correspondingly modified.

The question of the stability of standing spin density waves, at least insofar as correlation effects are ignored, is in principle answerable from IV-90 (with  $\omega = 0$ ). When solved, this equation yields the eigenvalues,  $\epsilon_i$  and eigen functions  $\mathcal{F}_i^-(x, q_i, \omega)$  characterizing the standing spin waves. By symmetry,  $\mathcal{F}_i^+$  and  $\mathcal{F}_i^\downarrow$  for each mode are obtained from

$$\mathcal{F}_i^+(x, q_i, \omega) = -\mathcal{F}_i^\downarrow(x, q_i, \omega) = \frac{1}{2} \mathcal{F}_i^-(x, q_i, \omega) \quad (\text{IV-91})$$

and the consequent change in energy density is computed from IV-74 disregarding, of course, terms quadratic in the  $\mathcal{F}'$ 's. Unfortunately, due to the complexity of IV-90 in the case of Coulomb interactions, this program has not yet been carried out. In view of this circumstance, the repulsive long-range Coulomb interaction is often replaced by a repulsive (short-range) delta function interaction - a case which can be solved. Since the Coulomb interaction is actually shielded at large distances by the dielectric behaviour of the medium, it is hoped that some features of the true situation are contained in this counterfeit model. With

$$f(q) = A > 0 \quad (\text{IV-92})$$

equation IV-90, when integrated over velocity space, yields the eigenvalue equation

$$1 + \frac{g^2 A}{2\hbar} \int d^3v \frac{F_0(\underline{v} + \frac{\hbar \underline{q}}{m}) - F_0(\underline{v})}{\underline{v} \cdot \underline{q} + \frac{\hbar q^2}{2m}} = 0 \quad (\text{IV-93})$$

At zero temperature, this reduces to

$$\frac{1-A'}{A'} = \frac{1-k^2}{2k} \log \left| \frac{1+k}{1-k} \right| \quad (\text{IV-94})$$

where  $A'$  is a positive constant times  $A$ , and

$$k \equiv \frac{\hbar q}{2m v_f} \quad (\text{IV-95})$$

From IV-94, it is seen that a single solution,  $q(A)$ , exists for all repulsive interaction strengths,  $A$ , in excess of some  $A_{\min}$ , with no solution for weaker or attractive interactions. The corresponding eigen function is

$$\mathcal{I}_1^- = \text{const} \frac{[F_0(\underline{v} + \frac{\hbar}{m} \underline{q}) - F_0(\underline{v})]}{\underline{v} \cdot \underline{q} + \frac{\hbar q^2}{2m}} \quad (\text{IV-96})$$

The energy calculation for this case has been carried out by Yoshimori (42), who finds that the energy increases for all interaction strengths capable of supporting a standing spin wave. Thus, for delta-function interactions at least, the spin wave state is unstable. Further work is clearly required to settle this issue. In particular the change in the "correlation energy" (see Chapter VII) attending a spin wave must also be taken into account.

In conclusion, we have seen that the introduction of exchange vastly increases the complexity of the equilibrium and non-equilibrium properties of spatially homogeneous systems. Thus, when we subsequently describe the equilibrium state of a spatially uniform or quasi-uniform system by IV-81, and assume it to be paramagnetic, we do so with some reservation. The system may in fact be ferromagnetic, be described by another solution to IV-76, or even possess standing spin density waves under certain conditions of density, temperature and interaction strength.



#### D. Quantum Hydrodynamics

The next topic of interest is how the exchange terms in the second quantum Vlasov equation modify the hydrodynamical transport equations derived in Section III-D. To explore this question, it is only necessary to compute the first three velocity space moments of these terms and add them to the corresponding equations: III-46, III-47 and III-48. For simplicity, we ignore the question of spin transport and deal with the "normal" case defined in IV-63.

Using the form IV-68 of the second quantum Vlasov equation, we can easily show that the mass conservation equation (III-56) is unchanged when exchange is included. Introducing IV-63 into IV-68 and integrating over  $\underline{v}_1$  yields the exchange term (dropping the subscript "norm")

$$\frac{ig^2 N}{2(2\pi)^3 \hbar} \int d^3 v_1 d^3 x_2 d^3 v_2 d^3 q f(q) \left[ e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_2, t) \right. \\ \left. - \tilde{F}^{(1)}(\underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, t) - e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2 - \frac{\hbar}{m} \underline{q}) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_2, t) \tilde{F}^{(1)}(\underline{x}_2, \underline{v}_1, t) \right] \quad (\text{IV-97})$$

which should be added to III-46. However, making the variable change

$\underline{v}_1' \equiv \underline{v}_1 + \frac{\hbar}{m} \underline{q}$  in the first term of IV-97 reveals that this expression is identically zero. Thus III-56 stands.

The momentum equation (III-74), on the other hand, is altered by exchange and in a somewhat complicated fashion. Multiplying IV-68 by the momentum component  $m v_1^M$  and integrating over  $\underline{v}_1$  leads to the exchange correction

$$-\frac{ig^2 N m}{2(2\pi)^3 \hbar} \int d^3 v_1 d^3 x_2 d^3 v_2 d^3 q f(q) \frac{\hbar}{m} q^M e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2 - \frac{\hbar}{m} \underline{q}) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_2) \tilde{F}^{(1)}(\underline{x}_2, \underline{v}_1) \quad (\text{IV-98})$$



to III-47. The complexity arises from the non-locality of this term which can be made apparent by repeating the calculation with the equivalent form, IV-67, of the second quantum Vlasov equation. In this way we find that IV-98 can also be written

$$-\frac{ig^2m}{\hbar} \int d^3v_1 v_1^M \sum_{n=1}^{\infty} \frac{1}{n!} \left(-\frac{i\hbar}{m}\right)^n \left[ \frac{\partial^n \phi^{exch}(\underline{x}_1, \underline{v}_1, t)}{\partial x_1^K \partial x_1^L \dots} \frac{\partial^n \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t)}{\partial v_1^K \partial v_1^L \dots} \right. \\ \left. - \frac{\partial^n \phi^{exch}(\underline{x}_1, \underline{v}_1, t)}{\partial v_1^K \partial v_1^L \dots} \frac{\partial^n \tilde{F}^{(1)}(\underline{x}_1, \underline{v}_1, t)}{\partial x_1^K \partial x_1^L \dots} \right] \quad (IV-99)$$

where

$$\phi^{exch}(\underline{x}_1, \underline{v}_1, t) = -\frac{N}{2} \int d^3v' f\left(\frac{m}{\hbar}(\underline{v}' - \underline{v}_1)\right) \tilde{F}^{(1)}(\underline{x}_1, \underline{v}', t) \quad (IV-100)$$

Due to the velocity dependence of the exchange potential, spatial derivatives of all (odd) orders contribute to IV-99, which is tantamount to non-locality.

Considerable simplification naturally results if we restrict our attention to systems which are spatially slowly varying so that only the  $n=1$  term in IV-99 need be retained. Such a restriction is in the spirit of the macroscopic nature of the hydrodynamic equations and, in fact, may be thought of as a redefinition of what we mean by macroscopic.

Thus, in place of IV-99 we consider

$$-g^2 \int d^3v v^M \left( \frac{\partial \phi^{exch}}{\partial x^K} \frac{\partial \tilde{F}^{(1)}}{\partial v^K} - \frac{\partial \phi^{exch}}{\partial v^K} \frac{\partial \tilde{F}^{(1)}}{\partial x^K} \right) \quad (IV-101)$$

Making use of IV-100, this reduces (after a few manipulations) to

$$\frac{\partial}{\partial x^K} \left[ \frac{g^2}{2N} \int d^3v d^3v' v^M f\left(\frac{m}{\hbar}(\underline{v}' - \underline{v})\right) (N \tilde{F}^{(1)}(\underline{x}, \underline{v}', t)) \frac{\partial}{\partial v^K} (N \tilde{F}^{(1)}(\underline{x}, \underline{v}, t)) \right] \\ + \frac{\partial}{\partial x^M} \left[ \frac{g^2}{4N} \int d^3v d^3v' f\left(\frac{m}{\hbar}(\underline{v}' - \underline{v})\right) (N \tilde{F}^{(1)}(\underline{x}, \underline{v}', t)) (N \tilde{F}^{(1)}(\underline{x}, \underline{v}, t)) \right] \quad (IV-102)$$

Following the development of Section III-D, we now introduce the ansatz, III-66, of local thermodynamic equilibrium. In so doing, we must make use of the fact that the imaginary part of  $\tilde{F}^{(1)}$ , being of quantum mechanical origin, is a function of spatial gradients of the Hamiltonian, IV-65, and vanishes if these gradients vanish. This may be deduced from the structure of the Generalized Poisson Bracket and will be explicitly demonstrated in Chapter V. Thus, in the spirit of the quasi-homogeneous hypothesis implicit in our retention of only the  $n=1$  term of IV-99\*, we are justified in replacing  $\tilde{F}^{(1)}$  by  $\text{Re } \tilde{F}^{(1)}$  in IV-102, thereby enabling us to apply III-66 directly. By the same token, in making the association, III-66, only the gradient independent part,  $\tilde{F}_0^{(1) \prime}$ , of the known function,  $\tilde{F}^{(1) \prime}$ , should be used. Specifically, let  $\tilde{F}_0^{(1) \prime}$  be the solution of the classical Poisson Bracket equation

$$\left\{ \tilde{F}_0^{(1) \prime}(\underline{x}, \underline{v}, t), H_{\text{NORM}}^{(1)}(\underline{x}, \underline{v}, t) \right\}_{\text{PB}}^{(1)} = 0 \quad (\text{IV-103})$$

appropriate to a local temperature  $T(\underline{x}, t)$  and density  $\langle n(\underline{x}, t) \rangle$ , with  $H_{\text{NORM}}^{(1)}$  given by IV-64. Then, in IV-102, we make the association

$$\tilde{F}^{(1)}(\underline{x}, \underline{v}, t) = \tilde{F}_0^{(1) \prime}(\underline{x}, \underline{v} - \langle \underline{u}(\underline{x}, t) \rangle, t) \quad (\text{IV-104})$$

Since the gradient-independent solution of IV-103 must be identical to that of a spatially uniform system, we can write down  $\tilde{F}_0^{(1) \prime}$  immediately from the results of the previous section. It is just the (normal) solution to IV-76, which in the Coulomb case is

$$\tilde{F}_0^{(1) \prime} \equiv \frac{1}{N} F_0(\underline{x}, \underline{v}, t) = \frac{2m^3}{N h^3} \left[ \exp \left( \frac{\frac{1}{2} m (\underline{v}^2 - \underline{v}_f^2 \langle n(\underline{x}, t) \rangle \tau(\underline{x}, t))}{h \tau(\underline{x}, t)} \right) + 1 \right]^{-1} \quad (\text{IV-105})$$

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\*This "quasi-homogeneous" assumption corresponds to treating the exchange part of the Hamiltonian "classically", since the integrand of IV-99 is  $\{ \tilde{F}^{(1)}, \phi^{\text{exch}} \}^{(1)}$  the first term of which is just the classical Poisson Bracket.

where

$$\frac{T}{\tau} = 1 + \frac{e^2}{\hbar \pi v_f \langle n \rangle, \tau=0} \ln \left[ (1.15) \left( \frac{\frac{1}{2} m v_f^2 \langle n \rangle, \tau=0}{\hbar \tau} \right) \right] \quad (\text{IV-106})$$

Introducing IV-104 into IV-102, we find after some algebra that the exchange-corrected form of the momentum equation III-74 is

$$\begin{aligned} m \langle n \rangle \left( \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \nabla \right) \langle \underline{u} \rangle + \nabla \cdot \langle \Pi' \rangle + \nabla \langle p'^{\text{exch}} \rangle \\ + \langle n \rangle \nabla g^2 \phi_T + \frac{\hbar^2}{4m} \nabla (\nabla^2 \langle n \rangle) = 0 \end{aligned} \quad (\text{IV-107})$$

where the exchange pressure,  $\langle p'^{\text{exch}} \rangle$ , is defined as

$$\begin{aligned} \langle p'^{\text{exch}}(\underline{x}, t) \rangle \equiv \int d^3 w \left[ \frac{m w^2}{6} \frac{\partial F_0(\underline{x}, \underline{w}, t)}{\partial (\frac{1}{2} m w^2)} + \frac{1}{4} F_0(\underline{x}, \underline{w}, t) \right] \\ \times \left[ g^2 \int d^3 w' f\left(\frac{m}{\hbar}(\underline{w}' - \underline{w})\right) F_0(\underline{x}, \underline{w}', t) \right] \end{aligned} \quad (\text{IV-108})$$

and  $F_0$  is given by  $(2N)$  times the solution of IV-76 in general, by IV-105 in the particular case of Coulomb interactions. The kinetic stress tensor,  $\langle \Pi' \rangle$ , is computed as before from III-73, using the specific form III-67 for  $\text{Re } \tilde{F}(\omega)$ .\*

To explore the nature of the exchange pressure, we concentrate on the Coulomb case, where IV-108 becomes

$$\begin{aligned} \langle p'^{\text{exch}} \rangle = \int_0^\infty d\omega \, 4\pi \omega^2 \left[ \frac{m \omega^2}{6} \frac{\partial F_0(\underline{x}, \underline{w}, t)}{\partial (\frac{1}{2} m \omega^2)} + \frac{1}{4} F_0(\underline{x}, \underline{w}, t) \right] \\ \times \left[ \frac{8\pi^2 e^2 \hbar^2}{m^2 \omega} \int_0^\infty d\omega' \, \omega' \ln \left| \frac{\omega + \omega'}{\omega - \omega'} \right| F_0(\underline{x}, \underline{w}', t) \right] \end{aligned} \quad (\text{IV-109})$$

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\*In so doing one must use the (exchange-corrected)  $\bar{F}_0$  just defined in place of III-68, as will be shown in Chapter V.



Integrating the first term by parts leads to the result

$$\begin{aligned} \langle p'^{\text{exch}} \rangle = & -\frac{1}{12} \left\{ \int_0^\infty dw \, 4\pi w^2 F_0(x, w, t) \left[ \frac{8\pi^2 e^2 \hbar^2}{m^2 w} \int_0^\infty dw' w' \ln \left| \frac{w+w'}{w-w'} \right| F_0(x, w', t) \right] \right\} \\ & + \frac{(4\pi)^3 e^2 \hbar^2}{6 m^2} \int_0^\infty dw \int_0^\infty dw' \frac{w^2 w'^2}{w^2 - w'^2} F_0(x, w, t) F_0(x, w', t) \end{aligned} \quad (\text{IV-110})$$

The second term of IV-110 vanishes by symmetric integration. From IV-75, the first term is recognized to be just 1/3 the exchange energy per unit volume. Using IV-83, we obtain the desired dependence of the exchange pressure on density and temperature

$$\begin{aligned} \langle p'^{\text{exch}}(\langle n \rangle, T) \rangle &= -\frac{1}{4} e^2 \langle n \rangle \left( \frac{3\langle n \rangle}{\pi} \right)^{1/3} \left( 1 + \frac{\chi^2}{6} \ln \left( \frac{\chi}{6.20} \right) \right) \\ &= \frac{1}{3} \langle \epsilon'^{\text{exch}} \rangle \end{aligned} \quad (\text{IV-111})$$

where the parameter  $\chi$  is defined by

$$\frac{\pi \hbar^2 T}{\left[ \frac{\pi^2 \hbar^2}{2m} \left( \frac{3\langle n \rangle}{\pi} \right)^{2/3} \right]} \equiv \chi \left[ 1 - \frac{e^2 m}{\pi^2 \hbar^2 \left( \frac{3\langle n \rangle}{\pi} \right)^{1/3}} \ln \left( \frac{\chi}{1.14} \right) \right] \quad \chi \ll 1 \quad (\text{IV-112})$$

It is of interest to compare the (negative) exchange pressure with the (positive) kinetic stress term  $\nabla \cdot \langle \pi' \rangle$  as computed from III-73 and III-67. In the absence of spatial gradients of the self-consistent field,  $\nabla \cdot \langle \pi' \rangle$  becomes the gradient of the kinetic pressure,  $p'^{\text{kin}}$ , given by 2/3 the kinetic energy per unit volume (cf. IV-83):

$$\langle p'^{\text{kin}} \rangle = \frac{2}{3} \langle \epsilon'^{\text{kin}} \rangle = \frac{1}{5} \frac{\pi^2 \hbar^2}{m} \langle n \rangle \left( \frac{3\langle n \rangle}{\pi} \right)^{2/3} \left( 1 + \frac{5}{12} \chi^2 \right) \quad (\text{IV-113})$$



Addition of IV-111 and IV-113 shows that the total pressure vanishes when

$$\langle n \rangle_{p=0} = \frac{125}{192} \frac{m^3 e^6}{\pi^5 \hbar^6} \left( \frac{1 + \frac{\chi^2}{6} \ln\left(\frac{\chi}{6.20}\right)}{1 + \frac{5}{12} \chi^2} \right)^3 \quad (\text{IV-114})$$

and goes negative for lower densities. Such behaviour of the equation of state is generally indicative of either a phase transition, a breakdown in the viability of the approximation procedure, or (more likely) both. For the electron gas, whose density is conventionally expressed in terms of the dimensionless parameter

$$r_s \equiv \left( \frac{4\pi}{3\langle n \rangle} \right)^{1/3} \frac{m e^2}{\hbar^2} \quad (\text{IV-115})$$

the criterion IV-114, when evaluated at zero temperature ( $\chi \rightarrow 0$ ) becomes

$$r_s)_{p=0} = 4.8 \quad (\text{IV-116})$$

a value approximately characteristic of the conduction electrons in alkali metals (lithium = 3.22, cesium = 5.57).\*

Turning finally to the energy transport equation, we must consider in place of IV-101 the exchange correction

$$-g^2 \int d^3v \frac{v^2}{2} \left( \frac{\partial \phi^{\text{exch}}}{\partial \chi^K} \frac{\partial \tilde{F}^{(1)}}{\partial v^K} - \frac{\partial \phi^{\text{exch}}}{\partial v^K} \frac{\partial \tilde{F}^{(1)}}{\partial \chi^K} \right) \quad (\text{IV-117})$$

to III-48. Proceeding analogously to the treatment of the momentum correction, we find (delegating the lengthy but straightforward calculational details to Appendix B) that the exchange-corrected form of the energy

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\*Speculation as to whether such transport anomalies are to be taken seriously in the case of metals must naturally await the introduction of entropy production via the collision integral derived in Chapter VIII and, more importantly, the inclusion of the electron-phonon interaction.

transport equation, III-76, is

$$\begin{aligned}
 m \langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \left( \langle \bar{\epsilon}' \rangle^{kin} - \frac{\hbar^2}{4m^2 \langle n \rangle} \nabla^2 \langle n \rangle \right) + \langle \pi' \rangle \cdot \underline{\nabla} \langle \underline{u} \rangle \\
 + \frac{\hbar^2}{4m} \nabla^2 \langle n \rangle \underline{\nabla} \cdot \langle \underline{u} \rangle + \langle \rho'^{exch} \rangle \underline{\nabla} \cdot \langle \underline{u} \rangle + \langle \epsilon'^{exch} \rangle \underline{\nabla} \cdot \langle \underline{u} \rangle \\
 + \underline{\nabla} \cdot \langle \underline{q}' \rangle = 0
 \end{aligned}
 \tag{IV-118}$$

where  $\langle \epsilon'^{exch} \rangle$ , the (ensemble averaged) expectation value of the exchange energy per unit volume in the moving (Lagrangian) frame is given by IV-75:

$$\langle \epsilon'^{exch} \rangle \equiv -\frac{1}{4} \int d^3 w F_0(\underline{x}, \underline{w}, t) \left[ g^2 \int d^3 w' f\left(\frac{m(\underline{w}' - \underline{w})}{\hbar} F_0(\underline{x}, \underline{w}', t)\right) \right] \tag{IV-119}$$

the remainder of the notation being identical to that of III-76.

Equation IV-118 is a rather surprising result in view of the way the exchange energy enters. The anomaly can be made more manifest by using the mass continuity relation III-56 in the form

$$\underline{\nabla} \cdot \langle \underline{u} \rangle = -\frac{1}{\langle n \rangle} \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \langle n \rangle \tag{IV-120}$$

to rewrite the exchange energy term as:

$$\begin{aligned}
 \langle \epsilon'^{exch} \rangle \underline{\nabla} \cdot \langle \underline{u} \rangle = m \langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \left( \frac{\langle \epsilon'^{exch} \rangle}{m \langle n \rangle} \right) \\
 - \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \langle \epsilon'^{exch} \rangle
 \end{aligned}
 \tag{IV-121}$$

The first term of IV-121 is just the total derivative of the exchange energy per unit mass which is what one would naturally expect to be added to the first term of IV-118. The second term of IV-121 is wholly unexpected.

While a full study of the implications of IV-118 lies beyond the scope of the present work, we will take a step in that direction by deriving from this equation the adiabats of a quasi-homogenous degenerate system with

Coulomb interactions. In the absence of significant inhomogeneity, the kinetic stress tensor  $\langle \pi' \rangle$  is diagonal, the elements being just the kinetic pressure IV-113. Using IV-111, IV-113, IV-120, and the notation

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \nabla \quad (\text{IV-122})$$

IV-118 can be written in the form (dropping the primes)

$$\frac{D}{Dt} \ln \langle \bar{E}^{kin} \rangle^{3/2} = \left( 1 + 2 \frac{\langle \bar{E}^{exch} \rangle}{\langle \bar{E}^{kin} \rangle} \right) \frac{D}{Dt} \ln \langle n \rangle \quad (\text{IV-123})$$

where

$$\langle \bar{E}^{exch} \rangle = -\frac{3}{4m} e^2 \left( \frac{3\langle n \rangle}{\pi} \right)^{1/3} \left( 1 + \frac{\chi^2}{6} \ln \left( \frac{\chi}{6.20} \right) \right) \quad (\text{IV-124})$$

$$\langle \bar{E}^{kin} \rangle = \frac{3\pi^2 \hbar^2}{10 m^2} \left( \frac{3\langle n \rangle}{\pi} \right)^{2/3} \left( 1 + \frac{5}{12} \chi^2 \right) \quad (\text{IV-125})$$

$\chi$  being defined in IV-112. IV-123 is then integrated to yield the desired relation between  $\chi$  and  $\langle n \rangle$  :

$$\int_{\chi_0^2}^{\chi^2} \frac{d(\chi'^2)}{1 + \frac{\chi'^2}{6} \ln \left( \frac{\chi'}{6.20} \right)} \approx \chi^2 - \chi_0^2 = \frac{24 e^2 m}{\pi^2 \hbar^2} \left( \frac{\pi}{3} \right)^{1/3} \left( \frac{1}{\langle n \rangle^{1/3}} - \frac{1}{\langle n_0 \rangle^{1/3}} \right) \quad (\text{IV-126})$$

where  $(\chi_0, \langle n_0 \rangle)$  define the adiabat and use has been made of the smallness of  $\chi$  at low temperatures.

For comparison, we can recover from IV-126 the adiabat in the absence of exchange by setting  $e^2 = 0$  and observing from IV-112 that

$$\chi \xrightarrow[e^2 \rightarrow 0]{} \frac{\pi \hbar^2 T}{\left[ \frac{\pi^2 \hbar^2}{2m} \left( \frac{3\langle n \rangle}{\pi} \right)^{2/3} \right]} \quad (\text{IV-127})$$



yielding just the usual free particle result

$$\chi^2 = \chi_0^2 \quad \text{or} \quad \frac{T}{T_0} = \left( \frac{\langle n \rangle}{\langle n_0 \rangle} \right)^{2/3} \quad (\text{IV-128})$$

A particularly striking feature of IV-126 vis-à-vis IV-128 is noted by concentrating on the adiabat defined by  $T_0 = 0$  (for a given  $\langle n_0 \rangle$ ). In the absence of exchange, IV-128 states that this adiabat is also an isotherm, meaning that the ground states of the system at different densities are adiabatically connected. IV-126, on the other hand, indicates that when exchange is included, this apparently is no longer the case. Further study of this point is clearly required.

As an application of IV-126, we will conclude this section by computing the effect of exchange on sound propagation in an electron gas. We consider a uniform gas at ambient density  $n_0$  and temperature  $T_0$ , with a consequent  $\chi_0$  as implicitly defined in IV-112. By linearizing the three hydrodynamic equations about these values, we obtain in the usual fashion a wave equation for the density perturbation,  $n_1$ :

$$\frac{\partial^2 n_1}{\partial t^2} = c^2(n_0, \chi_0) \nabla^2 n_1 \quad (\text{IV-129})$$

where the square of the sound velocity is given by

$$m c^2(n_0, \chi_0) \equiv \left. \frac{dp^{\text{total}}(n, \chi)}{dn} \right|_{\substack{n=n_0 \\ \chi=\chi_0}} = \left[ \left. \frac{\partial p^{\text{total}}}{\partial n} \right|_{\chi} + \left. \frac{\partial p^{\text{total}}}{\partial \chi} \right|_n \frac{d\chi}{dn} \right]_{\substack{n=n_0 \\ \chi=\chi_0}} \quad (\text{IV-130})$$

The total pressure appearing in IV-130 is the sum of the kinetic and exchange pressures as defined in IV-111 and IV-113.  $\chi$  is connected to  $n$  via the adiabatic equation of state IV-126. Making use of these relations and



the definition IV-115, we obtain the desired result:

$$\frac{C^2}{C_f^2} = 1 + \frac{5}{12} \chi_o^2 - \frac{3 r_{s_o}}{4^{1/3} \pi^2} \left[ 1 + \frac{\chi_o^2}{36} \ln \left( \left( \frac{\chi_o}{6.20} \right)^2 \right) \right] + \frac{r_{s_o}^2}{2 \pi^4 4^{2/3}} \left[ 1 + \ln \left( \left( \frac{\chi_o}{6.20} \right)^2 \right) \right] \quad (\text{IV-131})$$

where  $C_f^2$ , the square of the zero-temperature sonic velocity in the absence of exchange, is given by

$$C_f^2 \equiv \frac{4^{2/3} \pi^2 e^4}{3 r_{s_o}^2 \hbar^2} \quad (\text{IV-132})$$

The second term of IV-131 represents the non-zero temperature correction to this value which would occur in the absence of exchange. The remaining terms are exchange corrections. The most noticeable feature of these exchange terms is the logarithmic singularity of the last term at zero temperature ( $\chi_o \rightarrow 0$ ), which has the consequence that at any density, a critical temperature  $T_c$  exists such that sound waves cannot propagate (i.e.  $C^2 < 0$ ) for  $T_o < T_c$ . To obtain  $T_c$  as a function of  $r_{s_o}$ , we first obtain the root of IV-131 which, for small  $\chi$ , occurs at

$$r_{s_o} \Big|_{C^2=0} \cong \frac{4^{1/3} \pi^2}{\sqrt{\ln(1/x)}} \quad (\text{IV-133})$$

Inserting this relation into the definition IV-112 leads to the desired result:

$$\frac{k T_c}{\left( \frac{m e^4}{2 \hbar^2} \right)} = \frac{1}{\pi^3} \alpha^2 e^{-\alpha^2} \left[ 1 + \alpha + \frac{\ln 1.14}{\alpha} \right] \quad (\text{IV-134})$$

where

$$\alpha \equiv \frac{4^{1/3} \pi^2}{r_{s_0}} = \frac{15.7}{r_{s_0}} \quad (\text{IV-135})$$

$T_c$  is a quite sensitive function of  $r_{s_0}$  as may be seen in Table 1.

TABLE 1

Density Dependence of  $T_c$

$r_{s_0}$	2	3	4	5	6
$T_c$ °K	$4.4 \times 10^{-21}$	$1.1 \times 10^{-6}$	$7.4 \times 10^{-2}$	10.8	135

It should be emphasized that the foregoing result will most likely be significantly altered when correlations are taken into account (i.e. the third stage of approximation). This alteration will arise from two sources. First, viscosity and heat flow terms will appear in the hydrodynamic equations. Second, the total pressure will contain a new term arising from the density and temperature dependent "correlation energy" considered in Chapter VII. Since it is impossible to estimate the nature of such correlation effects at this point, the foregoing calculation should be interpreted as merely an indication of possible anomalies in the transport properties of an electron gas at extremely low temperatures. It is nevertheless interesting to have observed how the inclusion of exchange can radically alter the macroscopic behaviour of a many-Fermion system.

With the possible exception of the present section, the results obtained thus far are for the most part not new. In addition to the basic papers of von Roos (10,13,14), quantum mechanical Boltzmann equations have been studied, for example, by Landau (43), Goldstone and Gottfried (44), and Ehrenreich and Cohen (45), although the scope and depth of such studies are quite limited in comparison to the present work. In the remainder of the dissertation, we will break fresh ground by applying the formalism thus far developed to a detailed study of two problems of widespread theoretical interest -- the statistical model of the atom and the properties of a spatially uniform electron gas. As will be pointed out in the concluding chapter, these applications apparently just scratch the surface of potential utility of the formalism. It is hoped that the degree of generality maintained to this point (and henceforth to be abandoned) together with these two illustrative examples will facilitate further applications of the theory.



## Chapter V Plasma Theory of the Many-Electron Atom

### A. Introduction and Background

Some thirty-five years ago, Thomas (46) and Fermi (47) independently proposed a model of the atom which, although based on a number of simplifying assumptions, has proved extremely useful in the calculation of many properties of complex atomic systems. The success of the consequent Thomas-Fermi (TF) statistical model\* and the fact that alternative approaches based on a consideration of an N-electron Schroedinger equation involve a prohibitively greater degree of labor have led many investigators to attempt improvements of the model. Until recently, such improvements have been generally proposed on the basis of plausible extensions of the TF "approach", which we shall now briefly review.

The atom, assumed for simplicity to be spherically symmetric, is viewed in the TF model as consisting of spherical shells over which the electrostatic potential is approximately constant but which contain a sufficient number of electrons so that statistical methods can be applied. For an isolated atom in its ground state, the electrons in each shell are then assumed to constitute a totally degenerate electron gas at zero temperature, whose kinetic energy density,  $\epsilon^{kin}(r)$ , is related to the particle density,  $n(r)$ , by the usual relation

$$\epsilon^{kin}(r) = \frac{3}{10} (3\pi^2)^{2/3} \frac{\hbar^2}{m} n^{5/3}(r) \quad (V-1)$$

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\*Comprehensive reviews of the TF model and its various elaborations may be found in the tracts of March (48), Gombas (49), and Corson (50).



The electrostatic potential at  $r$  has two components: the nuclear potential  $\phi_N(r)$ , and a self-consistent field,  $\phi_{scf}(r)$ , related to  $n(r)$  by Poisson's equation.

$$\nabla^2 \phi_{scf} = 4\pi e n(r) \quad (V-2)$$

The total energy of the atom is then assumed to arise from these three sources, and thus to be given by the volume integral

$$E_{TOTAL} = \int d^3r \left\{ \epsilon^{kin}(r) - e n(r) \phi_N(r) - \frac{1}{2} e n(r) \phi_{scf}(r) \right\} \quad (V-3)$$

Minimization of the total energy with respect to arbitrary variations of  $n(r)$ ; subject, however, to the differential constraint V-2 and the normalization condition

$$\int d^3r n(r) = N \quad (V-4)$$

leads directly to the TF relation between the density and total electrostatic potential

$$n(r) = \frac{8\pi}{3h^3} (2me)^{3/2} (\phi(r) - \phi_0)^{3/2} \quad (V-5)$$

( $\phi_0$  being a Lagrange multiplier determined from V-4) which when combined with V-2 defines the model.

A first modification was proposed by Fermi and Amaldi (51) who, observing that the Poisson equation V-2 implies an interaction of each electron with itself, suggested in effect that this equation be replaced by

$$\nabla^2 \phi_{scf} = \frac{N-1}{N} 4\pi e n(r) \quad (V-6)$$

which approximately remedies this situation.

Dirac (52) added to the energy V-3 a term representing the exchange energy density and obtained in this fashion a modification of V-5:

$$n(r) = \frac{8\pi}{3h^3} (2me)^{3/2} \left[ a + (\phi(r) - \phi_0 + a^2)^{1/2} \right]^3 \quad (V-7)$$

where

$$a = (2me^3)^{1/2} / h \quad (V-8)$$

The so-called Thomas-Fermi-Dirac (TFD) model which results has been extensively applied. Arguments for ignoring the Fermi-Amaldi correction if exchange is included have been given by Jensen (53).

In the same vein, still another energy term, the so-called "correlation energy", representing the difference between the exact energy density of a (spatially homogeneous) electron gas and that given by the kinetic and exchange energy terms, has been added to V-3 by various authors. Since expressions for the correlation energy are only available in the high (Gell-Mann and Brueckner (54)) and low (Wigner (55)) density limits, an interpolation formula must be used at intermediate densities as in the work of Lewis (56). The Fermi-Amaldi correction is generally ignored in such calculations for reasons similar to those advanced in the TFD model.

Relativistic effects, which may be expected to play a significant role for very heavy atoms, have been explored (independently of other corrections) by several authors. Gilvarry (57), for example, considers in place of V-5 the relation

$$n(r) = \frac{8\pi}{3h^3} (2me)^{3/2} \left\{ E_0 - mc^2 + e\phi(r) + \left[ (E_0 - mc^2 + e\phi(r))^2 - \left( e r \frac{d\phi}{dr} \right)^2 \right] (2mc^2)^{-1} \right\}^{3/2} \quad (V-9)$$

( $E_0$  being a Lagrange multiplier determined from the normalization), which is based on an expression for the density of states derived from the single-particle Dirac equation by Rudkj bing (58).

In studies of the equation of state of highly compressed atoms, extensions of the TF model to non-zero temperatures are required. A modification of V-5, obtained by deriving the low temperature correction to V-1 from the non-zero temperature Fermi-Dirac distribution, was given by Marshak and Bethe (59) and was subsequently used in the equation of state work of Feynman, Metropolis and Teller (60). A similar treatment of the exchange correction was presented by Yokota (38) which, being based on the Fermi-Dirac distribution rather than IV-81, is incomplete. This state of affairs was corrected by Umeda and Tomishima (61).

It should be noted that the foregoing modifications all share a common defect with the TF model: they are quasi-classical inasmuch as quantum mechanics enters only via the use of Fermi-Dirac statistics in determining the dependence of the energy density on  $n(r)$ . Indeed, quantum mechanics per se is never introduced, only quantum statistics. This neglect is a consequence of the underlying assumption of the TF approach, viz. that the electrons may locally be considered as equivalent to a uniform gas at the same density, the wave functions of which are just plane waves. Due to the presence of potential gradients, however, plane waves are not an adequate approximation as was pointed out by Weizsacker (62), who proposed a modification of V-5 containing terms explicitly dependent on density gradients. The quantum (or "inhomogeneity" correction as it is often called) correction of Weizsacker was challenged on various grounds by several authors. Most detailed numerical studies of the TF model have consequently



ignored the question of quantum corrections, not because they are expected to be unimportant but rather because of the uncertainty as to the proper one to choose.

This unsatisfactory state of affairs emphasized the need for a systematic derivation of the model and its corrections from a complete quantum many-body theory, and resulted in a recent renewed interest in the theoretical foundations of the statistical model.

The first step in this direction had been taken by Dirac (52), who rewrote the Hartree-Fock equations in terms of the density matrix and, by making certain plausible assumptions about the distribution of electrons in phase space, succeeded in obtaining the TF model with an additional exchange term (the TFD model mentioned previously) in the limit of vanishing inhomogeneity. Subsequent investigations, most notably those of Kompaneets and Pavlovskii (63) and Golden (64), have generally followed Dirac's lead in the sense that quasi-classical approximations to the density matrix are studied. In particular, systematic expansions in  $\hbar$  have been developed which simultaneously generate both exchange and quantum corrections -- a procedure first suggested by Theis (65). A somewhat different but equivalent scheme was proposed by Kirzhnits (66). By assuming that the occupation number of each single-particle state depended on the expectation value of the Hamiltonian in that state, he was able to derive the TF model at non-zero temperatures.

Since these approaches were rooted in the Hartree-Fock approximation, however, they were unable to include correlation effects, i.e. deviations from Hartree-Fock. This defect motivated Baraff and Borowitz (67) to attack the problem from the standpoint of the Green's function formulation

of the quantum many-body problem. Expansion of the Green's function in powers of  $\hbar$  led indeed to the TF model in lowest order and to the quantum and exchange corrections in higher orders. Their work was limited to zero temperature, although use of the techniques due to Martin and Schwinger (68) can presumably allow an extension of the method to non-zero temperatures. In a subsequent paper, Baraff (69) attempted to include correlation effects by abandoning the ansatz that the two-particle Green's function can be decomposed into a (symmetrized) product of single-particle Green's functions, in close analogy to the quantum BBGKY hierarchy underlying our method. His results were later refuted by DuBois and Kivelson (70) who, also using a Green's function approach, concluded that the Lewis procedure mentioned earlier was in essence correct. Non-zero temperatures were formally included in the DuBois-Kivelson approach, but no attempt was made to derive the consequent corrections to the model, and it appears difficult to do so. In common with the previous studies based on the density matrix, relativistic effects were totally excluded.

There are, we feel, several unsatisfactory features in the foregoing studies. First, the role of the Fermi-Amaldi self-energy correction is nowhere discussed. This is particularly difficult to do in the Green's function approaches since they are based in essence upon a consideration of a spatially infinite though inhomogeneous electron gas, appearances to the contrary notwithstanding. Second, the question of how quantum, exchange, correlation, etc. corrections influence the boundary conditions on the model is generally ignored. To amplify this remark, it must be noted that the TF equation for the self-consistent electrostatic potential, even when corrected for various effects, possesses a family of solutions

corresponding to atoms in various states of compression. To single out the solution appropriate to an isolated atom, for example, one must be able to compute the pressure at the atomic boundary for each member of the family, the desired solution being that characterized by a vanishing of this quantity. Consequently, alterations of the boundary conditions play a marked, if indirect, role in practical applications of the theory.

Third, the perturbation procedure by which corrections to the TF potential are obtained is inconsistent inasmuch as the self-consistency of this potential is violated in each stage of approximation -- a point we will clarify later. Fourth, extensions of these methods to non-zero temperatures have only been achieved at the expense of considerable and, we feel, undue effort. This is a manifestation of what is perhaps the greatest drawback of approaches which proceed from inherently quantum mechanical formulations of the many-body problem and attempt to study quasi-classical physical situations, viz., the obscurity with which the correspondence principle is cloaked by the formalism. An unfortunate consequence of this obscurity is the sacrifice of the analytical and conceptual simplicity inherent in the Thomas-Fermi approach. As a result, the procedure for obtaining quantum and exchange corrections in more complex situations (such as atoms with net orbital angular momentum, for example) is a very difficult task, in spite of the fact that the TF model in such cases can be immediately written down from simple physical considerations.

The present formulation of the quantum many-body problem, due to its manifest exploitation of classical concepts and language, is particularly well suited to the present problem. Furthermore, since statistical mechanics has been introduced from the start, considerations of temperature are



already included. In Section B, the TF and TFD models are immediately obtained from the first and second quantum Vlasov equations (respectively) by going to the classical limit and thus replacing the Generalized Poisson Brackets by ordinary Poisson Brackets. The role of the Fermi-Amaldi correction in these models is also clarified. A straightforward expansion of the q.m.d.f. in powers of  $\hbar$  generates the quantum corrections to these models. In Section C, the hydrodynamic equations developed in Chapter IV are used to obtain an expression for the pressure at the atomic boundary which yields the equation of state for the atom and, as a special case, the boundary condition appropriate to an isolated atom. In Section D, a perturbation method is introduced by which approximate numerical solutions of the model can be obtained in terms of quadratures of tabulated functions. Expressions are derived for the radii of isolated atoms and the zero temperature equation of state of compressed matter in terms of these quadratures. Section E calls attention to Appendix A, where the efficacy of our approach is demonstrated by calculating for the first time the quantum and exchange corrections to the TF model of atoms with net orbital angular momentum. A new problem, plasma oscillations of a many-electron atom, is formulated but not solved in Section F. The relation of this problem to the hydrodynamical studies of Wheeler and Fireman (71) and Wakano (72) is briefly discussed. Although correlation and relativistic effects are not included in the present work, we indicate in the final section the lines along which the formalism can be extended to these cases. While lowest order relativistic corrections can probably be included quite readily, a connection between the correlation question and contemporary difficulties in classical plasma theory emerges which is difficult to reconcile with the simplicity of the procedure employed by Lewis and apparently justified in the study of DuBois and Kivelson.

## B. Derivation of Model

We shall begin by showing how the TF-Amaldi and TFD models follow immediately from the classical limits of the first and second quantum Vlasov equations respectively. It should be recalled that these equations are formally equivalent at zero temperature to the Schroedinger equation in the Hartree and Hartree-Fock approximations.

The time independent\* first quantum Vlasov equation appropriate to a spherically symmetric neutral atom consisting of  $Z$  electrons and an infinitely heavy point nucleus is obtained from III-14, III-15, and III-13. It is simply

$$\left\{ \tilde{F}^{(0)}(\underline{x}, v), H_{scF}(\underline{x}, v) \right\}_{G.P.B.}^{(1)} = 0 \quad (V-10)$$

where (in spherical coordinates)

$$H_{scF} = \frac{1}{2} m v^2 - \frac{Z e^2}{r} + e^2 \phi^{scF}(r) \quad (V-11)$$

and

$$\phi^{scF}(r) = \frac{Z-1}{Z} \int d^3 r' \frac{1}{|\underline{r}-\underline{r}'|} \int d^3 v' Z \tilde{F}^{(0)}(\underline{r}', v') \quad (V-12)$$

If, for simplicity, we introduce the definitions

$$\begin{aligned} F(\underline{r}, v) &\equiv Z \tilde{F}^{(0)}(\underline{r}, v) \\ U(r) &\equiv -\frac{Z e^2}{r} + e^2 \phi^{scF}(r) \\ \epsilon &\equiv \frac{1}{2} m v^2 + U(r) \end{aligned} \quad (V-13)$$

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\*The time independent form is used because the atom is assumed to be in thermal equilibrium. Non-equilibrium processes will be discussed later.

and operate on V-12 with the Laplacian, one obtains

$$\left\{ F, \epsilon \right\}_{G.P.B.}^{(1)} = 0 \quad (V-14)$$

and

$$\nabla^2 U = -4\pi e^2 \frac{Z-1}{Z} \int d^3 r' F(r, r') + 4\pi Z e^2 \delta(r) \quad (V-15)$$

where

$$U(r) \underset{r \rightarrow 0}{=} -\frac{Z e^2}{r} \quad (V-16)$$

The normalization of F is

$$\int d^3 v d^3 r F(r, v) = Z \quad (V-17)$$

so that at the boundary of the atom ( $r=R$ ) integration of V-15 yields

$$\left. \frac{dU}{dr} \right|_{r=R} = \frac{e^2}{R^2} \quad (V-18)$$

If we now take the classical limit of V-14, the Generalized Poisson Bracket becomes an ordinary Poisson Bracket as shown earlier. The solution ( $F_0$ ) of V-14 in this limit is, as is well known, any functional of the single-particle energy,  $\epsilon$ . To determine which functional to choose, one appeals (as in Chapter III) to the quantum-mechanical H-theorem or ensemble theory and obtains, naturally, the Fermi-Dirac distribution:

$$F_0(\epsilon) = \frac{2m^3}{h^3} \left[ \exp\left(\frac{\epsilon - \lambda}{kT}\right) + 1 \right]^{-1} \quad (V-19)$$

Equations V-15, V-19 and the associated boundary conditions are precisely the Thomas-Fermi-Amaldi model generalized to non-zero temperature. We have



demonstrated, therefore, that this model is nothing more or less than treating the atom as a spatially inhomogeneous classical plasma obeying Fermi-Dirac statistics -- hence the title of the present chapter. The pressure at the boundary of the atom is obtained simply from the hydrodynamic equation III-74 which states that in the classical limit, ( $\hbar \rightarrow 0$ ), the stress tensor defined by

$$\langle \pi_{(r)}^{ij} \rangle \equiv \int d^3v \, m v^i v^j F_0(r, v) \quad (V-20)$$

must be equal to the externally applied stresses at the boundary if hydrostatic equilibrium is to be attained. Since  $F_0$ , as given by V-19, is spherically symmetric in velocity space, this tensor is diagonal and isotropic. The consequent hydrostatic pressure at R is obtained trivially from V-20 and V-19 if the temperature of the boundary, T, is sufficiently low so that the electrons at the surface are still highly degenerate. The result is

$$\rho(R, T) = \frac{4 \cdot 2^{1/2} m^{3/2}}{15 \pi^2 \hbar^3} (\lambda - U(R, T))^{5/2} \left[ 1 + \frac{5\pi^2}{8} \left( \frac{kT}{\lambda - U(R, T)} \right)^2 \right] \quad (V-21)$$

where  $U(R, T)$  is the solution of V-15, V-16 and V-18. The isolated atom is obtained by letting  $T \rightarrow 0$  and demanding that the pressure vanish at the boundary, yielding simply

$$U(R) = \lambda \quad (V-22)$$

or, equivalently, that the density vanishes at the surface.

In precisely the same fashion, we may obtain the TFD model from the classical limit of the second quantum Vlasov equation.\* Comparing IV-64, IV-65 and IV-54 with III-14, III-15 and III-13, we note first that the Fermi-Amaldi  $Z-1/Z$  factor no longer occurs so that V-15 and V-17 are

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\*We assume the spin-density to be everywhere zero.

replaced by

$$\nabla^2 U = -4\pi e^2 \int d^3 v' F(r, v') + 4\pi z e^2 S(r) \quad (V-23)$$

and

$$\left. \frac{dU}{dr} \right|_{r=R} = 0 \quad (V-24)$$

respectively. Furthermore, it is seen that in going to the classical limit by replacing the G.P.B. by an ordinary Poisson bracket, the equation determining the consequent  $F_0$  is now

$$\left\{ F_0, \epsilon_{TFD} \right\}_{P.B.} = 0 \quad (V-25)$$

where the exchange-modified single-particle energy is given by

$$\epsilon_{T.F.D.} = \frac{1}{2} m v^2 + U(r) - \frac{2\pi e^2 \hbar^2}{m^2} \int d^3 v' \frac{F_0(r, v')}{|v - v'|^2} \quad (V-26)$$

the Fourier transform (III-39) of the Coulomb interaction having been inserted into the exchange term IV-66.

As before, any functional of  $\epsilon_{TFD}$  will satisfy V-25, the choice again to be determined, in general, by statistical considerations. Local maximization of the entropy subject to the constraint of constant total energy yields in place of V-19, the relation (cf. IV-76)

$$\begin{aligned} F_0(\epsilon_{T.F.D.}) &= \frac{2m^3}{h^3} \left[ \exp\left(\frac{\epsilon_{T.F.D.} - \lambda}{kT}\right) + 1 \right]^{-1} \\ &\equiv \frac{2m^3}{h^3} \left[ \exp\left(\frac{\frac{1}{2} m v^2 + U(r) - \frac{2\pi e^2 \hbar^2}{m^2} \int d^3 v' \frac{F_0(\epsilon_{TFD}(r, v'))}{|v - v'|^2} - \lambda}{kT}\right) + 1 \right]^{-1} \end{aligned} \quad (V-27)$$

which, when combined with V-23, constitutes the TFD as generalized to arbitrary temperature by Umeda and Tomishima (61). Concentrating for simplicity on the zero-temperature case, we have already shown in Section IV-C that V-27 can be solved in this limit to yield\*

$$F_0(r, v) = \begin{cases} 2 \frac{m^3}{h^3} & v \leq v_f(r) \\ 0 & v \geq v_f(r) \end{cases} \quad (V-28)$$

where in place IV-80, we have

$$\frac{1}{2} m v_f^2 - \frac{e^2 m}{\pi \hbar} v_f + U(r) - \lambda = 0 \quad (V-29)$$

Solving this quadratic equation for  $v_f$  (keeping only the positive square root in the usual fashion -- see Plaskett (73)), we obtain from V-28 an expression for the density

$$n(r) = \frac{8\pi}{3} \frac{m^3}{h^3} v_f^3 = \frac{8\pi}{3 h^3} (2m)^{3/2} \left[ \frac{(2m)^{1/2} e^2}{h} + \left( \frac{2me^4}{h^2} + \lambda - U(r) \right)^{1/2} \right]^3 \quad (V-30)$$

which constitutes the TFD model, V-7. The pressure at the atomic boundary is again obtained from the hydrodynamic momentum equation -- IV-107 in the present case. The net stress tensor now contains a contribution from the exchange pressure

$$\langle \pi_{net}^{ij} \rangle = \int d^3v m v^i v^j F(r, v) + \langle p'_{exch} \rangle \delta^{ij} \quad (V-31)$$

which has been evaluated for the Fermi-Dirac distribution in IV-111. The kinetic part of the stress tensor is trivially evaluated and we find (using

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\*As is to be expected, V-28 can be obtained without recourse to statistical mechanics. We have already demonstrated (see IV-24) that this is a direct consequence of the form, IV-1, of the Hartree-Fock wave function coupled with the requirement that the energy be minimal. The same result was obtained by Theis (65) as a consequence of the "idempotency" of the density matrix.



V-30) that the total surface pressure is

$$p(R, T=0) = \frac{\pi^3 \hbar^2}{15 m} \left(\frac{3}{\pi}\right)^{5/3} [n(R)]^{5/3} - \frac{e^2}{4} \left(\frac{3}{\pi}\right)^{1/3} [n(R)]^{4/3} \quad (V-32)$$

where  $N(R)$  is related to  $U(R)$  through V-30. Since  $N(R)$  is always greater than zero (see V-30), the pressure can only vanish if

$$n(R) = \frac{125 m^3 e^6}{192 \pi^5 \hbar^2} \quad (V-33)$$

a condition which could have been anticipated from IV-114.

The TFD model has thus been found to follow directly from the "classical" limit of the second quantum Vlasov equation -- classical in the sense that only the lowest order spatial gradients occurring in the Generalized Poisson Bracket are retained. To generate quantum corrections to the foregoing models, one has only to include in a systematic fashion progressively higher order constituents of the G.P.B. The procedure for doing so is immediately apparent from the form IV-67 of the second quantum Vlasov equation, which in the present problem becomes

$$\begin{aligned} \tilde{U} \cdot \nabla_{\tilde{x}} F - \frac{1}{m} \nabla_{\tilde{x}} U \cdot \nabla_{\tilde{v}} F &= \frac{i\hbar}{2m} \nabla_{\tilde{r}}^2 F + \frac{i}{\hbar} \sum_{n=2}^{\infty} \frac{1}{n!} \left(\frac{-i\hbar}{m}\right)^n \frac{\partial^n U}{\partial x^k \partial x^l \dots} \frac{\partial^n F}{\partial v^k \partial v^l \dots} \\ &+ \frac{i}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left(\frac{-i\hbar}{m}\right)^n \left[ \frac{\partial^n \phi^{exch}}{\partial x^k \partial x^l \dots} \frac{\partial^n F}{\partial v^k \partial v^l \dots} - \frac{\partial^n \phi^{exch}}{\partial v^k \partial v^l \dots} \frac{\partial^n F}{\partial x^k \partial x^l \dots} \right] \end{aligned} \quad (V-34)$$

where

$$\phi^{exch}(x, v) = -2\pi \frac{e^2 \hbar^2}{m^2} \int d^3 v' \frac{F(x, v')}{|x - x'|^2} \quad (V-35)$$

and

$$\nabla^2 U = -4\pi e^2 \int d^3 r' F(\underline{r}, \underline{r}') + 4\pi z e^2 S(\underline{r}) \quad (V-36)$$

Noting that the right hand side of V-34 contains all powers of  $\hbar$  starting with the first, we introduce the formal expansions

$$F = \sum_{n=0}^{\infty} \hbar^n F_n \quad \phi^{\text{exch}} = \hbar^2 \sum_{n=0}^{\infty} \hbar^n \phi_n^{\text{exch}} \quad (V-37)$$

into this equation, considering U, for the moment, to be a given potential. Matching the coefficients of equal powers of  $\hbar$  leads to the chain of equations:

0th order

$$(\underline{r} \cdot \nabla_{\underline{r}} - \frac{1}{m} \nabla_{\underline{r}} U \cdot \nabla_{\underline{r}}) F_0 = 0 \quad (V-38)$$

1st order

$$(\underline{r} \cdot \nabla_{\underline{r}} - \frac{1}{m} \nabla_{\underline{r}} U \cdot \nabla_{\underline{r}}) F_1 = \frac{i}{2m} \left[ \nabla_{\underline{r}}^2 F_0 - \frac{1}{m} \frac{\partial^2 U}{\partial x^k \partial x^L} \frac{\partial^2 F_0}{\partial v^k \partial v^L} \right] \quad (V-39)$$

2nd order

$$(\underline{r} \cdot \nabla_{\underline{r}} - \frac{1}{m} \nabla_{\underline{r}} U \cdot \nabla_{\underline{r}}) F_2 = \frac{i}{2m} \left[ \nabla_{\underline{r}}^2 F_1 - \frac{1}{m} \frac{\partial^2 U}{\partial x^k \partial x^L} \frac{\partial^2 F_1}{\partial v^k \partial v^L} \right] \quad (V-40)$$

$$- \frac{1}{6m^3} \frac{\partial^3 U}{\partial x^k \partial x^L \partial x^M} \frac{\partial^3 F_0}{\partial v^k \partial v^L \partial v^M} + \nabla_{\underline{r}} \phi_0^{\text{exch}} \cdot \nabla_{\underline{r}} F_0 - \nabla_{\underline{v}} F_0 \cdot \nabla_{\underline{r}} \phi_0^{\text{exch}}$$

etc., which generates all the  $F_n$  as functionals of (the as yet unspecified)  $F_0$  and various gradients of U. The potential, U, is then rendered self-consistent by means of V-36.

Generally, the series V-37 are truncated at some power of  $\hbar$ . Defining the  $p$ th approximation to F as follows (we indicate here the explicit

dependence of the  $F_n$  on  $U$ )

$$F^{(p)}(U; r, \psi) \equiv \sum_{n=0}^p \hbar^n F_n(U; r, \psi) \quad (V-41)$$

the corresponding approximation,  $U^{(p)}$ , to the potential is then determined from

$$\nabla^2 U^{(p)} = -4\pi e^2 \int d^3v F^{(p)}(U^{(p)}; r, \psi) \quad (V-42)$$

a procedure which guarantees its self-consistency at every state of approximation. The normalization of the  $F^{(p)}$  and boundary conditions on  $U^{(p)}$  are naturally the same for all  $p$ , viz.

$$\int d^3v d^3r F^{(p)}(U^{(p)}(r); r, \psi) = Z \quad (V-43)$$

and

$$U^{(p)}(r) \underset{r \rightarrow 0}{=} -\frac{Ze^2}{r} \quad ; \quad \left. \frac{dU}{dr} \right|_{r=R} = 0 \quad (V-44)$$

All that remains then is to specify  $F_0$ . This, however, is a trivial question since  $F_0$  is just the distribution function which one would have in the absence of quantum or exchange corrections; namely, that which is appropriate to the Thomas-Fermi model considered previously (without, of course, the Fermi-Amaldi correction).

Thus

$$F_0 = \frac{2m^3}{h^3} \left[ \exp\left(\frac{\frac{1}{2}mv^2 + U(r) - \lambda}{kT}\right) + 1 \right]^{-1} \quad (V-45)$$

A few points must be noted. First, the chemical potential,  $\lambda$ , occurring in V-45 is implicitly dependent on  $\hbar$ . It is carried through the



calculation as an unspecified constant, eventually to be determined from V-43. Thus, V-41 and V-42 should be more properly written as

$$F^{(p)}(U; \lambda; r, v) \equiv \sum_{n=0}^p \hbar^n F_n(U; \lambda; r, v) \quad (V-46)$$

and

$$\int d^3v d^3r F^{(p)}(U^{(p)}(r); \lambda^{(p)}; r, v) = Z \quad (V-47)$$

It is readily seen that the homogeneous solutions to V-39, V-40, etc. correspond simply to the corrections to  $\lambda$  of order  $\hbar$ ,  $\hbar^2$ , etc. Second, it is important to call attention to the fact that in our scheme, the lowest order equations correspond to the TF rather than the TFD model. An alternative chain of equations for the  $F_n$  could have indeed been obtained by postponing the consideration of the  $\hbar$  dependence of the exchange potential in the same manner as that of the self-consistent field. Although the two approaches are formally equivalent if one goes to infinite order in  $\hbar$  (i.e.  $p \rightarrow \infty$  in V-41), the effect for any finite  $p$  is to introduce, in the latter approach, exchange corrections of order higher than  $\hbar^p$ . Since we shall presently find that the quantum corrections in any order contain terms of the same form and magnitude as the exchange correction in that order, it is artificial to treat the two types of corrections differently -- notwithstanding the fact that they arise from different physical origins. A conclusive justification for our procedure is obtained by re-writing V-34 in terms of the dimensionless variables appropriate to the problem (to be introduced shortly). For the present purpose, we need only note that the characteristic distance scales as  $Z^{-1/3}$ , velocity as  $Z^{2/3}$ , energy as  $Z^{4/3}$ , and

$$F_n \propto Z^{-n/3}$$

Introduction of these relations into V-34 reveals that our procedure is a consistent expansion in a dimensionless parameter proportional to  $Z^{-1/3}$ , whereas a method proceeding from the TFD model is not. This is an important point since the TFD solutions have physically unrealistic features (such as the finite density V-33 at the boundary of a free atom) which are not expected to persist when quantum effects are taken into account.

In the present work, we limit our considerations to order  $\hbar^2$ , and hence must solve V-39 and V-40. The solution of these equations is algebraically straightforward and thus relegated to Appendix C. There we consider in fact the more general problem characterized by a single particle Hamiltonian which is an arbitrary function of  $\underline{x}$  and  $\underline{v}$  rather than V-13. Our motivation for doing this is both to facilitate application of the formalism to a wider class of problems and to indicate how solutions can be obtained to higher orders in  $\hbar$ . The result for  $F^{(2)}$  (not to be confused with  $\tilde{F}^{(2)}$ , the doublet q.m.d.f.) is

$$F^{(2)}(U; \underline{x}, \underline{v}) = \left\{ F_0(\epsilon) - \frac{i\hbar}{2} \frac{d^2 F_0}{d\epsilon^2} (\underline{v} \cdot \nabla_{\underline{x}} U) - \frac{\hbar^2}{4m} \frac{d^2 F_0}{d\epsilon^2} \nabla^2 U \right. \\ \left. - \frac{\hbar^2}{6} \frac{d^3 F_0}{d\epsilon^3} \left[ \underline{v} \cdot \nabla_{\underline{x}} (\underline{v} \cdot \nabla_{\underline{x}} U) + \frac{1}{m} (\nabla U)^2 \right] - \frac{\hbar^2}{8} \frac{d^4 F_0}{d\epsilon^4} (\underline{v} \cdot \nabla_{\underline{x}} U)^2 \right. \\ \left. - \frac{2\pi e^2 \hbar^2}{m^2} \frac{d F_0}{d\epsilon} \int \frac{d^3 v'}{|\underline{v} - \underline{v}'|^2} F_0(\underline{x}, \underline{v}') \right\}_{\epsilon = \frac{1}{2} m v^2 + U(\underline{x})} \quad (V-48)$$

where

$$F_0(\epsilon) \equiv \frac{2m^3}{h^3} \left[ \exp\left(\frac{\epsilon - \lambda}{kT}\right) + 1 \right]^{-1} \equiv \frac{2m^3}{h^3} f_0(\epsilon) \quad (V-49)$$

Inserting this result into the Poisson equation V-42 and performing the angular integrations in velocity space, yields, after some algebra,

$$\begin{aligned} \nabla^2 U^{(2)} = & \frac{-4e^2(2m)^{3/2}}{3\pi\hbar^3} \left\{ I_{3/2}(U^{(2)}-\lambda^{(2)}, T) - \frac{\hbar^2}{16m} \nabla^2 U^{(2)} I_{-1/2}(U^{(2)}-\lambda^{(2)}, T) \right. \\ & \left. - \frac{\hbar^2}{64m} (\nabla^2 U^{(2)})^2 I_{-3/2}(U^{(2)}-\lambda^{(2)}, T) + \frac{3e^2(2m)^{1/2}}{2\pi\hbar} [I_{1/2}(U^{(2)}-\lambda^{(2)}, T)]^2 \right\} \end{aligned} \quad (V-50)$$

where the Fermi-Dirac integrals,  $I_n$ , are defined as

$$I_n(x, T) \equiv - \int_0^\infty dw w^n \left\{ \frac{d}{dy} \left[ e^{\frac{y}{kT}} + 1 \right]^{-1} \right\}_{y=x+w} \quad (V-51)$$

and have the low temperature expansions

$$I_n(x, T) = (-x)^n \left[ 1 + \frac{\pi^2}{6} n(n-1) \left( \frac{kT}{x} \right)^2 + O\left( \left( \frac{kT}{x} \right)^4 \right) \right] \quad (V-52)$$

Solving V-50 for  $\nabla^2 U^{(2)}$  gives

$$\nabla^2 U^{(2)} = \frac{-4e^2(2m)^{3/2}}{3\pi\hbar^3} I_{3/2}(U^{(2)}-\lambda^{(2)}, T) \left\{ \frac{1 + \frac{3}{2} \frac{e^2(2m)^{1/2}}{\pi\hbar} \cdot \frac{I_{1/2}^2(x, T)}{I_{3/2}(x, T)} - \frac{\hbar^2}{64m} (\nabla^2 U^{(2)})^2 \frac{I_{-3/2}(x, T)}{I_{3/2}(x, T)}}{1 - \frac{e^2(2m)^{1/2}}{6\pi\hbar} I_{-1/2}(x, T)} \right\} \quad (V-53)$$

$-x = \lambda^{(2)} - U^{(2)}$

Since the denominator effectively introduces terms of order beyond  $\hbar^2$ , we must expand it to obtain the final result

$$\nabla^2 U^{(2)} = \frac{-4e^2(2m)^{3/2}}{3\pi\hbar^3} I_{3/2}(U^{(2)}-\lambda^{(2)}, T) \left\{ \underset{\text{T.F.}}{1} + \underset{\text{EXCH.}}{\frac{3e^2(2m)^{1/2}}{2\pi\hbar} \left[ \frac{I_{1/2}^2}{I_{3/2}} + \frac{1}{9} I_{-1/2} \right]} - \underset{\text{QUANTUM}}{\frac{\hbar^2}{64m} (\nabla^2 U^{(2)})^2 \frac{I_{-3/2}}{I_{3/2}}} \right\} \quad (V-54)$$

QUANTUM



which is the TF model generalized to arbitrary temperatures, and corrected for quantum and exchange effects to order  $\hbar^2$ . The physical origin of the correction terms is as indicated. In particular, note that a quantum correction appears which has the same form at zero temperature as the exchange correction but is smaller by a factor 1/9. To establish contact with previously published results, we pass to the limit of zero temperature and let

$$U^{(2)} \equiv U_0 + \hbar^2 U_2 \quad (V-55)$$

where  $U_0$  is the solution of the TF equation:

$$\nabla^2 U_0 = -\frac{4e^2}{3\pi\hbar^3} [2m(\lambda - U_0)]^{3/2} \quad (V-56)$$

Then, assuming  $\hbar^2 U_2 \ll U_0$  so that only lowest order terms are kept, we find for  $U_2$  the equation

$$\begin{aligned} -\nabla^2 U_2 + \frac{4me^2}{\pi\hbar^3} [2m(\lambda - U_0)]^{1/2} U_2 &= \frac{8m^2 e^4}{\pi^2 \hbar^6} (\lambda - U_0) \\ &\quad - \frac{me^2}{12\pi\hbar^3} [2m(\lambda - U_0)]^{-1/2} [4\nabla^2 U_0 + (\lambda - U_0)^{-1} (\nabla U_0)^2] \end{aligned} \quad (V-57)$$

which is identical, for example, to equation 4.15 of reference (67). We note and take exception to the fact that the perturbation procedure used to obtain V-57 from V-54, while no doubt justifiable as a method to facilitate numerical solution of the equations, nevertheless destroys the self-consistency of the model.

Finally, we make use of V-52 to obtain the lowest order temperature corrections and find

$$\begin{aligned} \nabla^2 U^{(2)}(r, T) &= -4 \frac{e^2 (2m)^{3/2}}{3\pi\hbar^3} (\lambda^{(2)} - U^{(2)})^{3/2} \left( 1 + \frac{\pi^2}{8} \left( \frac{\hbar T}{\lambda^{(2)} - U^{(2)}} \right)^2 \right) \left\{ 1 + \frac{5e^2 (2m)^{1/2}}{3\pi\hbar (\lambda^{(2)} - U^{(2)})^{1/2}} \right. \\ &\quad \times \left( 1 - \frac{7}{40} \pi^2 \left( \frac{\hbar T}{\lambda^{(2)} - U^{(2)}} \right)^2 \right) - \frac{\hbar^2 (\nabla U^{(2)})^2}{64m (\lambda^{(2)} - U^{(2)})^3} \left( 1 - \frac{\pi^2}{2} \left( \frac{\hbar T}{\lambda^{(2)} - U^{(2)}} \right)^2 \right) \left. \right\} \end{aligned} \quad (V-58)$$

In discussions of the TF model, it is customary to introduce the dimensionless variables

$$\lambda^{(2)} - V^{(2)} \equiv \frac{Ze^2}{r} \quad r \equiv bx \quad b \equiv \frac{1}{4} \left( \frac{9\pi^2}{2z} \right)^{1/3} \frac{\hbar^2}{me^2} = \frac{0.98534}{z^{1/3}} \frac{\hbar^2}{me^2} \quad (V-59)$$

in terms of which V-58 becomes simply

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \left( 1 + \frac{1}{2} \frac{t^2 x^2}{\phi^2} \right) \left\{ 1 + 10\alpha \left( \frac{x}{\phi} \right)^{1/2} \left[ 1 - \frac{7}{10} \frac{t^2 x^2}{\phi^2} \right] - \frac{\alpha}{4} \frac{(\phi - x\phi')^2}{x\phi^3} \left[ 1 - 2 \frac{t^2 x^2}{\phi^2} \right] \right\} \quad (V-60)$$

where we have introduced the additional definitions

$$T \equiv \left( \frac{2Ze^2}{\pi k b} \right) t \quad \alpha \equiv \frac{1}{12 z^{2/3}} \left( \frac{6}{\pi^2} \right)^{1/3} = \frac{0.0705}{z^{2/3}} \quad (V-61)$$

The boundary conditions on  $\phi$  are

$$\phi(0) = 1 \quad (V-62)$$

and

$$\phi(X) - X\phi'(X) = 0 \quad (V-63)$$

where  $X$  is the dimensionless radius of the atom.

To complete the model, it is necessary to determine the pressure at the atomic boundary since a one parameter\* family of solutions to V-60 exists which is consistent with the two point boundary conditions V-62 and V-63. This family characterizes the atom in different states of compression, the free atom being described by that (zero temperature) solution of V-60 whose surface pressure vanishes.

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\*Corresponding to different values of  $\phi'(0)$ , or, equivalently, the chemical potential.

### C. Theory of the Compressed Atom

The calculation of the pressure which must be exerted on the boundary of an atom in order to confine it to a sphere of radius  $R$  is greatly facilitated by the hydrodynamic theory developed in Chapter IV as has already been demonstrated in the case of the far simpler TF and TFD models. This is a particular advantage, we feel, of the present formulation since in conventional treatments (49), even in the absence of quantum corrections, one must compute the total energy of the atom as a function of  $R$  and then obtain the pressure from the derivative of this quantity. As one would expect on physical grounds, the volume integrals involved in such a procedure are ultimately reduced (generally after some labor) to surface integrals, thus enabling the pressure to be expressed entirely in terms of quantities evaluated at the atomic boundary. Our method circumvents this unnecessary and elaborate procedure.

Since we have shown that exchange corrections first appear in order  $\hbar^2$ , the hydrodynamic theory of Chapter IV which retained only the lowest order exchange term is correct to this order. In going to higher orders, more terms of IV-99 would naturally have to be introduced into the analysis, the procedure for doing so being clear from our previous work. It should be emphasized, however, that the exchange-independent quantum corrections to the hydrodynamic equations as developed in Section III-D are correct to all orders in  $\hbar$ .

We proceed from the momentum equation IV-107 which, when the convective velocity  $\langle \underline{u} \rangle$  is set equal to zero, becomes the equation of hydrostatic equilibrium. It is immediately apparent from this equation that at the atomic boundary ( $R$ ) the net stress tensor whose divergence must be



balanced by external forces (contained in the  $\nabla \phi_T$  term) is given by

$$\Pi_{NET}^{ij}(R) = \int d^3v m v^i v^j F(R, v) + \delta^{ij} \left( \langle p'^{exch}(R) \rangle + \frac{\hbar^2}{4m} \nabla^2 \langle n(R) \rangle \right) \quad (V-64)$$

To avoid unrewarding complications we will evaluate this quantity at zero temperature, the generalization to non-zero temperatures being straightforward.\* Recalling that  $\langle p'^{exch}(R) \rangle$  and  $\langle n(R) \rangle$  are obtained from  $F$ , a little care must be taken to insure that only corrections of order  $\hbar^2$  to the net stress tensor are included. We therefore rewrite V-64 as

$$\Pi_{NET}^{ij(2)}(R) = \int d^3v m v^i v^j F^{(2)}(R, v) + \delta^{ij} \left( \langle p'^{exch}(F_0(R, v)) \rangle + \frac{\hbar^2}{4m} \nabla^2 \langle n(F_0(R, v)) \rangle \right) \quad (V-65)$$

so there will be no confusion.

The leading contribution to  $\Pi$  comes from the  $F_0$  piece of the first term of V-65. Straightforward evaluation yields

$$\int d^3v m v^i v^j F_0 = \frac{4 \cdot 2^{1/2} m^{3/2}}{15 \pi^2 \hbar^3} (\lambda^{(2)} - U^{(2)}(R))^{5/2} \delta^{ij} \quad (V-66)$$

which is just the TF term, V-21.

Exchange corrections to  $\Pi$  come from two sources -- directly through the exchange pressure and indirectly through the exchange contribution to the kinetic stress tensor (i.e. the first term of V-65). The exchange pressure has already been computed for a Fermi-Dirac distribution in IV-111 and is

$$\langle p'^{exch}(F_0) \rangle = -\frac{1}{4} e^2 \left( \frac{3}{\pi} \right)^{1/3} \langle n(F_0) \rangle^{4/3} = -\frac{e^2 m^2}{3 \pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \quad (V-67)$$

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\*One note of caution, however. In using IV-111 for  $\langle p'^{exch} \rangle$ , the parameter  $\chi$  must be taken to be

$$\chi = \pi \hbar T [\lambda^{(1)} - U^{(1)}]^{-1}$$

rather than that obtained from the full IV-112. Use of IV-112 would introduce higher order corrections.

The exchange correction to the kinetic stress tensor as obtained from V-48 is

$$-\frac{2\pi e^2 \hbar^2}{m^2} \int d^3 v \, m v^i v^j \frac{dF_0(\epsilon)}{d\epsilon} \bigg|_{\epsilon = \frac{1}{2} m v^2 + U^{(2)}(R)} \int d^3 v' \, F_0(R, v') |v - v'|^{-2} = \frac{4 e^2 m^2}{3 \pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \delta^{ij} \quad (V-68)$$

Before computing the remaining (inhomogeneity) contributions, it is of value to collect the terms obtained thus far. Combining V-66, V-67 and

V-68, we have

$$\Pi_{NET}^{ij(2)} = \delta^{ij} \left( \frac{4 \cdot 2^{1/2} m^{3/2}}{15 \pi^2 \hbar^3} (\lambda^{(2)} - U^{(2)}(R))^{5/2} \left[ 1 + \frac{15 e^2 m^{1/2}}{4 \cdot 2^{1/2} \pi \hbar (\lambda^{(2)} - U^{(2)}(R))^{1/2}} \right] \right)$$

+ inhomogeneity correction

(V-69)

It is readily verified that these terms are in agreement with those obtained to the same order from the TFD expressions V-32 and V-30, which serves as a convenient check.

Turning finally to the quantum corrections, we will make extensive use of the boundary condition V-24 which enables us to ignore all terms proportional to  $\frac{dU}{dr}$ . Thus, the last term of V-65 reduces to

$$\delta^{ij} \frac{\hbar^2}{4m} \nabla^2 \langle n(F_0) \rangle = \delta^{ij} \frac{\hbar^2}{4m} \frac{(2m)^{3/2}}{3 \pi^2 \hbar^3} \left[ \nabla^2 (\lambda^{(2)} - U^{(2)}(R))^{3/2} \right] = \delta^{ij} \frac{\hbar^2 (2m)^{3/2}}{4m 3 \pi^2 \hbar^3} \left[ -\frac{3}{2} (\lambda^{(2)} - U^{(2)})^{1/2} \nabla^2 U^{(2)} \right]_{r=R} \quad (V-70)$$

which, by virtue of the Poisson equation V-54, becomes

$$\delta^{ij} \frac{\hbar^2}{4m} \nabla^2 \langle n(F_0) \rangle = \frac{4 m e^2}{3 \pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \quad (V-71)$$

terms of higher order having been dropped.

Similarly, we need only consider two of the inhomogeneity corrections to the kinetic stress tensor:

$$\int d^3v m v^i v^j \left( -\frac{\hbar^2}{4m} \nabla^2 U^{(2)} \frac{d^2 F_0}{d\epsilon^2} \right)_{\epsilon = \frac{1}{2} m v^2 + U^{(2)}} \quad (V-72)$$

and

$$\int d^3v m v^i v^j \left( -\frac{\hbar^2}{6} v^k v^l \frac{\partial^2 U^{(2)}}{\partial x^k \partial x^l} \frac{d^3 F_0}{d\epsilon^3} \right)_{\epsilon = \frac{1}{2} m v^2 + U^{(2)}} \quad (V-73)$$

since the others vanish at the boundary.

Evaluation of V-72 is straightforward and we find

$$\int d^3v m v^i v^j \left( -\frac{\hbar^2}{4m} \nabla^2 U^{(2)} \frac{d^2 F_0}{d\epsilon^2} \right)_{\epsilon = \frac{1}{2} m v^2 + U^{(2)}} = \frac{4 e^2 m^2}{3 \pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \delta^{ij} \quad (V-74)$$

V-73, on the other hand, is somewhat more involved. First, we note that as a consequence of the vanishing of  $\frac{dU^{(2)}}{dr}$  :

$$v^k v^l \frac{d^2 U^{(2)}}{dx^k dx^l} \Big|_{r=R} = \nabla^2 U^{(2)} \Big|_{r=R} \cdot \left( \frac{\underline{v} \cdot \underline{R}}{R} \right)^2 \quad (V-75)$$

Inserting this result into V-73 reveals that this tensor, though diagonal in a spherical coordinate system, is not isotropic, there being an additional purely radial stress component. Evaluating V-73 (making use as before of the leading term for  $\nabla^2 U^{(2)}$  from V-54), we find it becomes

$$-\frac{8 m^2 e^2}{9 \pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \delta^{ij} [1 + 2 \delta^{i1}] \quad (V-76)$$



where we have referred the stress tensor to a spherical coordinate system, the indices (1,2,3) now corresponding to the  $\hat{u}_r$ ,  $\hat{u}_\theta$ ,  $\hat{u}_\phi$  respectively. The consequent radial stress is thus

$$-\frac{8}{3} \frac{m^2 e^2}{\pi^3 \hbar^4} (\lambda^{(2)} - U^{(2)}(R))^2 \quad (V-77)$$

Combining V-71, V-74 and V-77 yields the striking result that the inhomogeneity correction to the surface pressure vanishes in order  $\hbar^2$ . It should be noted that the three terms whose mutual cancellation\* produces this result are each of the same magnitude as the exchange contributions V-67 and V-68.

The final desired result for the surface pressure  $p^{(2)}(R)$  is thus contained in V-69 and is

$$p^{(2)}(R) = \frac{4 \cdot 2^{1/2} m^{3/2}}{15 \pi^2 \hbar^3} (\lambda^{(2)} - U^{(2)}(R))^{5/2} \left[ 1 + \frac{15 e^2 m^{1/2}}{4 \cdot 2^{1/2} \pi \hbar (\lambda^{(2)} - U^{(2)}(R))^{1/2}} \right] \quad (V-78)$$

In terms of the dimensionless variables V-59, this becomes

$$\begin{aligned} p^{(2)}(X) &= \frac{Z^{10/3} e^6 m^4}{10 \pi (.88534)^4 \hbar^4} \left( \frac{\phi(X)}{X} \right)^{5/2} \left[ 1 + \frac{45}{4} \alpha \left( \frac{X}{\phi(X)} \right)^{1/2} \right] \\ &= 1.5 \times 10^{13} Z^{10/3} \left( \frac{\phi(X)}{X} \right)^{5/2} \left[ 1 + \frac{45}{4} \alpha \left( \frac{X}{\phi(X)} \right)^{1/2} \right] \text{ dynes/cm}^2 \end{aligned} \quad (V-79)$$

The boundary condition appropriate to the isolated atom is thus seen to be

$$\frac{\phi(X)}{X} = 0 \quad (V-80)$$

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\*This cancellation does not persist at non-zero temperatures, the sum of these terms then being

$$P_{inhomo} \approx -\frac{m^2 e^2}{\hbar^4} \cdot \frac{1}{6} (\hbar T)^2$$

which, from V-60, is tantamount to zero density at the surface.\*

The result, V-79, disagrees with the corresponding expression obtained by Kalitkin (74), who employed the method of Kirzhnits (66) to obtain quantum and exchange corrections to the TF model from the density matrix formalism. In particular, he concludes that the pressure vanishes for a non-zero value of the surface density which would result in a somewhat smaller radius of the isolated atom than would be obtained from V-80. While the equation for the electrostatic potential which he obtains is apparently equivalent to V-57 (as it must be), his expression for the pressure is obtained "with the help of equations analogous to the virial theorem in the TF model." The vagueness on this point and the extreme conciseness of his paper makes it difficult to evaluate the point of departure between our work and his.

#### D. Perturbation Technique for Approximate Solution of Model

Detailed numerical solution of the model lies beyond the scope of the present investigation since it is difficult to justify the extensive requisite computer time until the lowest order correlation and (for large  $Z$ ) relativistic corrections have also been included. Although we shall presently show that approximate solutions can be relatively simply obtained in terms of quadratures of tabulated functions from a perturbation analysis of V-60, there is some doubt as to the adequacy of this approximation since the corrections to the self consistent field become comparable to the unperturbed (TF) solution near the edge of the free atom. We therefore will formally carry out such an analysis, leaving the actual numerical evaluation of the quadratures to the interested reader.

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\*That is, assuming that the final term of V-60 does not blow up at large  $X$ , an assumption which is borne out if one uses the asymptotic form  $\phi \rightarrow \frac{144}{\chi^3}$ , of the TF potential to approximately evaluate it.

Restricting our consideration to the case where temperature corrections can be ignored, the basic equation of the model is V-60:

$$\begin{aligned}\frac{d^2\phi}{d\chi^2} &\equiv \phi'' = \frac{\phi^{3/2}}{\chi^{1/2}} \left\{ 1 + 10\alpha \left[ \left( \frac{\chi}{\phi} \right)^{1/2} - \frac{1}{40} \frac{(\phi - \chi\phi')^2}{\chi\phi^3} \right] \right\} \\ &\equiv \frac{\phi^{3/2}}{\chi^{1/2}} \left\{ 1 + \alpha f(\chi, \phi, \phi') \right\}\end{aligned}\tag{V-81}$$

with the general boundary conditions

$$\phi(0) = 1\tag{V-82}$$

$$\phi(X) - X\phi'(X) = 0\tag{V-83}$$

and in the particular case of the free atom (see V-80)

$$\phi(X_0) = X_0\phi'(X_0) = 0\tag{V-84}$$

where  $X$  and  $X_0$  are the dimensionless radii of the compressed and free atom respectively.

Turning first to the free atom, let  $\phi_0$  be the TF function defined by

$$\begin{aligned}\phi_0'' &= \frac{\phi_0^{3/2}}{\chi^{1/2}} & \phi_0(0) &= 1 & \lim_{\chi \rightarrow \infty} \phi_0(\chi) &= 0\end{aligned}\tag{V-85}$$

and define  $\eta$  :

$$\eta'' = \frac{3}{2} \left( \frac{\phi_0^{1/2}}{\chi^{1/2}} \right) \eta \quad \eta(0) = 0 \quad \eta'(0) = 1\tag{V-86}$$

in terms of  $\phi_0$ . Both  $\phi_0$  and  $\eta$ , as well as their first derivatives, have been tabulated by Gombas (p. 358 of reference (75)).



Setting

$$\phi(x) \equiv \phi_0(x) + \alpha h(x) \eta(x) \quad (V-87)$$

we find from V-81 that to lowest order in  $\alpha$ ,  $h(x)$  satisfies the equation

$$h'' + 2 \frac{\eta'}{\eta} h' = \frac{\phi_0^{3/2}}{\eta x^{1/2}} f(x, \phi_0, \phi_0') \quad (V-88)$$

Before integrating this equation, certain difficulties at very small  $x$  must be cited. Examination of V-81 reveals that for  $x$  less than a critical value,  $x_c$ , approximately given by

$$x_c \approx \frac{\alpha}{4} \quad (V-89)$$

the inhomogeneity correction drives the right-hand side negative which is tantamount to a (meaningless) negative density. Since V-89 corresponds to a distance of about 1.5% of the radius of the K-shell, the number of electrons contained in a sphere of this radius is certainly so small that the application of a statistical approach in this region is clearly insupportable. Relativistic effects also become important in this region. The breakdown then is not to be taken seriously. We therefore adopt the procedure\* of only applying V-81 for  $x \geq x_c$ , with a consequent alteration of V-82

$$\phi(x_c) = 1 \quad (V-90)$$

equivalent to excluding electrons from the region  $x < x_c$ . The effect of this procedure on the model at reasonable values of  $x$  is negligible.

Integrating V-88 and determining the integration constants from the boundary conditions V-82 and V-84 results in the following expression for

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\*For convenience, we will continue to formally integrate V-81 from the origin with the understanding that the above modification is to be made in any actual numerical integration.

the free-atom solution:

$$\phi(x) = \phi_0(x) - \phi_0(X_0) - 10\alpha\eta(x) \int_x^{X_0} \frac{g(x')}{\eta^2(x')} dx' \quad (V-91)$$

where

$$g(y) \equiv \int_0^y \left[ \eta\phi_0 - \frac{\eta(\phi_0 - x\phi'_0)^2}{40 (x\phi_0)^{3/2}} \right] dx \quad (V-92)$$

and  $X_0(\alpha)$  is implicitly determined from the relation

$$\alpha = \frac{\phi_0(X_0)\eta'(X_0) - \eta(X_0)\phi'_0(X_0)}{10 g(X_0)} \quad (V-93)$$

For the compressed atom, we require an expression for  $\phi(X)$  which when combined with V-79 yields the pressure as a function of atomic volume. Straightforward combination of V-83, V-87 and V-88 leads to

$$\frac{\phi(X)}{X} = \frac{\eta(X)\phi'_0(X) - \phi_0(X)\eta'(X) + 10\alpha g(X)}{\eta(X) - X\eta'(X)} \quad (V-94)$$

It is therefore seen that the equation of state of compressed matter can be obtained for all atomic numbers in this approximation by evaluating the single quadrature V-92. The convergence difficulties at small  $X$  mentioned earlier do not, incidentally, create any problems in computing  $g$ . Formal integration to the origin introduces an error in  $g$  of the order  $-\frac{1}{40}\alpha^{1/2}$  which negligibly alters V-94.

Since all physical properties of the model are derivable from  $F^{(2)}$  which, in turn, is determined by  $\phi$  and its first derivative, the problem is thus formally solved within the framework of the perturbation approximation.

#### E. Application of Method to Other Problems

The quasi-classical statistical methods developed in this chapter can, of course, be applied to a study of the equilibrium properties of spatially inhomogeneous interacting systems with more degrees of freedom and complexity than the spherical atom. Generally speaking, wherever the TF approach has been fruitfully applied, the expression for  $F^{(2)}$  derived in Appendix C coupled (if necessary) with the hydrodynamic analysis given earlier enables one to immediately correct the model for quantum and exchange effects. Furthermore, the uncorrected TF model itself (i.e.  $\bar{F}_0$ ) is obtained by the simple procedure of finding that functional of the classical constants of the single-particle motion which maximizes the (quantum-statistical) entropy\* subject to the constraints on the system. The analogue of the TFD model is similarly obtained by computing the "exchange potential" from the (given) particle interaction using IV-53 and applying a similar approach to the pseudo-classical problem defined by  $(H_{\text{classical}} + g^2 \phi^{\text{exch}})$ . Above all, it should be re-emphasized that the uncorrected TF "approach" to any problem is fully equivalent to viewing the system in question as a classical correlationless plasma obeying quantum statistics. The consequences of this observation will be discussed further in Sections F and G.

As an example of the efficacy of our approach, we have included in Appendix A a reprint of our original paper which forms the basis for the

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\*More properly, one should speak of minimizing the free energy.



present discussion. In it the quantum and exchange corrections to the statistical model of an atom with non-zero net orbital angular momentum has been derived for the first time. The motivation for this application was a remark in March's (48) review article indicating that such corrections may significantly alter the results of Sessler and Foley (76) who employed the TF and TFD models appropriate to such atoms to compute the quadrupole coupling constant and the magnetic field at the nucleus due to the orbital motion of the electrons. While a treatment which assigns such a manifestly "single-particle" property as the net orbital angular momentum "collectively" to the entire atom violates the shell structure known to characterize atoms and thus is a highly dubious approach, the necessary equations for those inclined to extend their work appear in our article. There is, however, a more intriguing question which could be answered from our results. Instead of arbitrarily requiring the atom to have zero net orbital angular momentum as is usually done, one should allow the model to generate net angular momentum if a state of lower energy is thus obtained. Specifically, one should compute the total energy of the atom as a function of  $L$  and then locate the minimum. While it is most likely that a non-rotating atom in fact has lowest energy, this is not manifestly obvious due to the complexity of the quantum and exchange corrections.

For the sake of completeness, it must be pointed out that the Fermi-Amaldi factors which appear in Appendix A are in error as the analysis of Section IV A in the present work was not available at the time it was written. Similarly unavailable was the general result of Appendix C which would have immensely simplified the algebra occasioned by the centrifugal potential.

Finally, it should be observed that in the spirit of viewing net orbital angular momentum as a collective property of the atom, one might also choose to treat the net spin in the same fashion. The method for generalizing our model to this case is simply to treat the two spin species as independent systems coupled through the net self-consistent field as shown in Chapter IV. The result of such a procedure would be the introduction of a new parameter -- essentially the ratio of the chemical potentials of the two species -- which would again be chosen from the standpoint of minimizing the total energy. In view of IV-86, it is highly likely that such a generalization would lend to a net non-zero spin density localized in the outer regions of the atom.

#### F. Non-Equilibrium Processes and Excited States

In addition to the ground state of a many-electron atom, the nature of the excited states is also of theoretical interest. Certainly the most important excited states are single-particle excitations in which the excitation energy is given to one or, less frequently, a few electrons. While such states are pure quantum mechanical and must be calculated from the Schroedinger or Dirac equations, the statistical model is still of great value in determining the potential to be used in such calculations. The work of Latter (77), for example, based on the TF and TFD potentials could thus be refined using the model derived herein.

The fact that the many-electron atom appears to be describable in its gross features as a classical plasma obeying Fermi statistics suggests the interesting possibility that modes of collective excitation may also exist in which the excitation energy is jointly shared by all or most of the

electrons. One such class of excitations has actually already been implicitly treated when the statistical model was generalized to non-zero temperatures. In contrast to these thermal excitations, however, modes of collective oscillation can also be anticipated. Such excitations have been studied in the hydrodynamic limit by several authors, most recently by Wheeler and Fireman (71) and Wakano (72). In these studies, the classical hydrodynamic equations have been applied to an inhomogeneous electron gas whose ambient density is that given by the TF model and whose equation of state is that characteristic of a totally degenerate free electron gas (i.e. IV-113). The results of this analysis enabled Wheeler and Fireman to compute a universal photo absorption cross-section for far ultraviolet and soft x-radiation due to such excitations. While their work can obviously be improved by using the quantum and exchange-corrected hydrodynamics developed in IV-D as well as the improved density expressions derived in the present chapter, there appear to be good reasons to doubt the validity of the hydrodynamic approximation itself -- a point which does not seem to have been considered by these authors. Specifically, as we discussed earlier, the criterion for the validity of hydrodynamics as applied to time-dependent processes is that the frequency of thermalizing (i.e. large momentum transfer) collisions should be large compared to the characteristic frequencies of these processes. A simple calculation reveals this not to be the case.

The characteristic oscillation frequencies are of the order of the classical plasma frequency appropriate to the mean electronic density in the atom. In particular, one finds (Jensen (73))

$$\omega_{osc} \approx \sqrt{\frac{4\pi \bar{n} e^2}{m}} \approx \frac{m e^4}{\hbar^3} \approx \frac{\sqrt{2}}{\pi} \quad (V-95)$$



The characteristic collision frequency can be estimated from the Rutherford cross-section for large angle scattering of an electron whose velocity is of the order of the average Fermi velocity:

$$\omega_{\text{coll}} \approx \bar{n} \bar{v}_f \sigma_{\text{RUTH.}}(\bar{v}_f, \theta > 45^\circ) \approx \frac{4 m e^4}{3\pi \hbar^3} \quad (\text{V-96})$$

Thus

$$\frac{\omega_{\text{coll}}}{\omega_{\text{osc}}} \approx \frac{1}{Z} \ll 1 \quad (\text{V-97})$$

which contradicts the assumption  $\omega_{\text{coll}} \gg \omega_{\text{osc}}$ . Even more important is the fact that the exclusion principle vastly inhibits collisions in a degenerate electron gas, effectively restricting them to occur between particles in the immediate vicinity of the Fermi surface. The net result of the exclusion principle would thus be to greatly enhance the inequality V-97.

Finally, there is the curious result obtained in IV-D, viz. that adiabatic inviscid oscillations in a zero temperature quasi-homogeneous electron gas are apparently impossible when exchange effects are included.

It seems clear, therefore, that collective oscillations of a many-electron atom must be studied in the collisionless rather than hydrodynamic approximation, a suggestion which to the best of our knowledge has not been made before.

The basic equation describing such plasma oscillations of the many-electron atom is the time-dependent second quantum Vlasov equation obtained by simply adding  $\partial F / \partial t$  to the left-hand side of V-34. Furthermore, since the oscillations are assumed to be a small perturbation to the equilibrium configuration, the linearized form should be used. Specifically,

let  $\bar{F}(x, y)$  and  $\bar{U}(r)$  denote the solutions of the time-independent V-34 and V-36, and let

$$F(x, y, t) \equiv \bar{F}(x, y) + f(x, y, t) \quad (V-98)$$

$$U(r, t) \equiv \bar{U}(r) + u(r, t) \quad (V-99)$$

where

$$\nabla^2 u = -4\pi e^2 \int d^3v f(x, y, t) + 4\pi e^2 \rho^{ext}(x, t) \quad (V-100)$$

Also let

$$\phi^{exch}(x, y, t) \equiv \bar{\phi}^{exch}(x, y) + \varphi^{exch}(x, y, t) \quad (V-101)$$

where

$$\bar{\phi}^{exch} \equiv -2\pi \frac{e^2 \hbar^2}{m^2} \int d^3v' \frac{\bar{F}(x, y')}{|y - y'|^2} \quad (V-102)$$

and

$$\varphi^{exch} \equiv -2\pi \frac{e^2 \hbar^2}{m^2} \int d^3v' \frac{f(x, y', t)}{|y - y'|^2} \quad (V-103)$$

Then we find for  $f$  the equation

$$\begin{aligned} \frac{\partial f}{\partial t} + y \cdot \nabla_x f - \frac{1}{m} \nabla_x \bar{U} \cdot \nabla_y f - \frac{1}{m} \nabla_x u \cdot \nabla_y \bar{F} &= \frac{i\hbar}{2m} \nabla_x^2 f \\ + \frac{i}{\hbar} \sum_{n=2}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n &\left[ \frac{\partial^n \bar{U}}{\partial x^k \partial x^l} \cdot \frac{\partial^n f}{\partial v^k \partial v^l} + \frac{\partial^n u}{\partial x^k \partial x^l} \cdot \frac{\partial^n \bar{F}}{\partial v^k \partial v^l} \right] \\ + \frac{i}{\hbar} \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{-i\hbar}{m} \right)^n &\left[ \frac{\partial^n \bar{\phi}^{exch}}{\partial x^k \partial x^l} \cdot \frac{\partial^n f}{\partial v^k \partial v^l} + \frac{\partial^n \varphi^{exch}}{\partial x^k \partial x^l} \cdot \frac{\partial^n \bar{F}}{\partial v^k \partial v^l} \right. \\ &\left. - \frac{\partial^n \bar{\phi}^{exch}}{\partial v^k \partial v^l} \cdot \frac{\partial^n f}{\partial x^k \partial x^l} - \frac{\partial^n \varphi^{exch}}{\partial v^k \partial v^l} \cdot \frac{\partial^n \bar{F}}{\partial x^k \partial x^l} \right] \end{aligned} \quad (V-104)$$

Considering  $\bar{U}$  and  $\mu$  to be given functions, we expand as before

$$f \equiv \sum_{n=0}^{\infty} \hbar^n f_n \quad (V-105)$$

and find the sequence of equations

$$\frac{\partial f_0}{\partial t} + \mathcal{L} \cdot \nabla_x f_0 - \frac{1}{m} \nabla_x \bar{U} \cdot \nabla_x f_0 - \frac{1}{m} \nabla_x \mu \cdot \nabla_x \bar{F}_0(\bar{U}, x, y) = 0 \quad (V-106)$$

$$\frac{\partial f_1}{\partial t} + \mathcal{L} \cdot \nabla_x f_1 - \frac{1}{m} \nabla_x \bar{U} \cdot \nabla_x f_1 - \frac{1}{m} \nabla_x \mu \cdot \nabla_x \bar{F}_1(\bar{U}, x, y) = \frac{i}{2m} \nabla_x^2 f_0 \quad (V-107)$$

$$\frac{\partial f_2}{\partial t} + \mathcal{L} \cdot \nabla_x f_2 - \frac{1}{m} \nabla_x \bar{U} \cdot \nabla_x f_2 - \frac{1}{m} \nabla_x \mu \cdot \nabla_x \bar{F}_2(\bar{U}, x, y) = \quad (V-108)$$

$$\begin{aligned} & \frac{i}{2m} \left[ \nabla_x^2 f_1 - \frac{1}{m} \frac{\partial^2 \bar{U}}{\partial x^k \partial x^l} \frac{\partial^2 f_1}{\partial v^k \partial v^l} - \frac{\partial^2 \mu}{\partial x^k \partial x^l} \frac{\partial^2 \bar{F}_1}{\partial v^k \partial v^l} \right] \\ & - \frac{1}{6m^3} \left[ \frac{\partial^3 \bar{U}}{\partial x^k \partial x^l \partial x^m} \frac{\partial^3 f_0}{\partial v^k \partial v^l \partial v^m} + \frac{\partial^3 \mu}{\partial x^k \partial x^l \partial x^m} \frac{\partial^3 \bar{F}_0}{\partial v^k \partial v^l \partial v^m} \right] \\ & + \nabla_x \bar{\phi}_0^{\text{exch}} \cdot \nabla_x f_0 + \nabla_x \phi_0^{\text{exch}} \cdot \nabla_x \bar{F}_0 - \nabla_x \bar{F}_0 \cdot \nabla_x \phi_0^{\text{exch}} - \nabla_x f_0 \cdot \nabla_x \bar{\phi}_0^{\text{exch}} \end{aligned}$$

etc., where the  $\bar{F}_n$  (and thus  $\bar{\phi}_0^{\text{exch}}$ ) have been computed up to  $n=2$  in V-48.

Truncating the chain at order  $\hbar^P$  and defining

$$f^{(P)} \equiv \sum_{n=0}^P \hbar^n f_n(\mu; x, y, t) \quad (V-109)$$

$\mu$  is then rendered self-consistent to this order

$$\nabla^2 \mu^{(P)} = -4\pi e^2 \int d^3 v f^{(P)}(\mu^{(P)}; x, y, t) + 4\pi e \rho^{\text{ext}}(x, t) \quad (V-110)$$

in direct analogy to the formalism of Section V-B.



Due to the fact that the classical problem of plasma oscillations in a strongly inhomogeneous system represents one of the frontiers of current research, the solution of even V-106 presents sufficient difficulty to probably render the calculation of quantum and exchange corrections to  $f_0$  unworthy of the effort involved. Since (in analogy to the static case) such corrections are likely to be small, most of the physics of the problem should be contained in V-106 together with an ad hoc quantization of the harmonic oscillator-like solutions derived therefrom.

#### G. Relativistic and Correlation Corrections

As indicated in Section D, one must be sure that all corrections to the model of order comparable to the  $\hbar^2$  quantum and exchange terms thus far derived are included before a detailed numerical investigation can be justified or, indeed, considered meaningful. While such filigree as retardation effects and spin-spin and hyperfine interactions can be rejected out-of-hand by the crudest order of magnitude estimates, small though significant corrections due to relativity and correlations (i.e. the inadequacy of the Hartree-Fock approximation) may be anticipated. The former of these effects alters the model in the inner regions of high  $Z$  atoms, the latter (most likely) in the low density outer regions of moderate and low  $Z$  elements.

Proceeding on the assumption that these effects will be small, we can compute them independently of the quantum and exchange corrections and hence need only concern ourselves with the problem of appropriately modifying the simple TF model with the understanding that all corrections will be linearly superposed in the final analysis. Specifically, what we strive for is a

corrected equation V-60 of the form

$$\frac{d^2\phi}{dx^2} = \frac{\phi^{3/2}}{x^{1/2}} \left\{ 1 + \frac{t^2}{2} \frac{x^2}{\phi^2} + \alpha(z) \left[ 10 \left( \frac{x}{\phi} \right)^{1/2} - \frac{1}{4} \frac{(\phi - x\phi')^2}{x\phi^3} \right] \right. \\ \left. + \beta(z) f_{rel.}(\phi, \phi', x) + \gamma(z) f_{corr.}(\phi, \phi', x) \right\} \quad (V-111)$$

where  $f_{rel.}$  and  $f_{corr.}$  are the as yet undetermined relativistic and correlation corrections which result to lowest order in the appropriate dimensionless perturbation parameters  $\beta$  and  $\gamma$ .

The realization that the TF model is equivalent to treating the atom as a classical inhomogeneous plasma obeying Fermi statistics considerably simplifies the foregoing task since one need only inquire how classical plasmas are corrected to lowest order for these effects.

Turning first to the relativistic question, we note that a relativistic generalization of the classical Vlasov equation (neglecting retardation) has been given by Clemmow and Wilson (79)\* which, in the absence of magnetic forces, can be written as

$$\frac{\partial F}{\partial t} + \left(1 + \frac{u^2}{c^2}\right)^{-1/2} \underline{u} \cdot \nabla_x F(x, u, t) - \frac{1}{m} \nabla_x U(x, t) \cdot \nabla_u F(x, u, t) = 0 \quad (V-112)$$

where we now work in a covariant phase space defined by  $\underline{x}$  and the reduced velocity,  $\underline{u}$ , given by

$$\underline{u} = \frac{\underline{v}}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (V-113)$$

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\*I am indebted to Dr. P. Burt for calling this paper to my attention.

It is easily verified that any functional of the argument

$$\epsilon(\underline{r}, \underline{u}) \equiv mc^2 \sqrt{1 + \frac{u^2}{c^2}} + U(\underline{r}) = \frac{mc^2}{\sqrt{1 - v^2/c^2}} + U(\underline{r}) \quad (\text{V-114})$$

is a time-independent solution of V-112, a result which could certainly have been anticipated on intuitive grounds.

In the entropy maximization, relativistic Fermi statistics must now, naturally, be employed. One then finds (see e.g. Ter Haar (27)) that

$$F(\underline{r}, \underline{u}) = \frac{2m^3}{h^3} \left[ \exp \left( \frac{mc^2(1 + \frac{u^2}{c^2})^{1/2} + U(\underline{r}) - mc^2 - \lambda}{kT} \right) + 1 \right]^{-1} \quad (\text{V-115})$$

At zero temperature, the case of interest here, V-115 yields for the density

$$n(\underline{r}) = \frac{8\pi}{3} \frac{m^3}{h^3} u_f^3(\underline{r}) \quad (\text{V-116})$$

where the reduced Fermi velocity is determined from

$$mc^2 \left( 1 + \frac{u_f^2}{c^2} \right)^{1/2} + U(\underline{r}) - mc^2 = \lambda \quad (\text{V-117})$$

Combining V-116 and V-117 gives the following expression for the density

$$n(\underline{r}) = \frac{(2m(\lambda - U(\underline{r})))^{3/2}}{3\pi^2 \hbar^3} \left\{ 1 + \frac{(\lambda - U(\underline{r}))}{2mc^2} \right\}^{3/2} \quad (\text{V-118})$$

which, when introduced into Poisson's equation, leads to the relativistic TF model:

$$\nabla^2 U = -\frac{4e^2}{3\pi \hbar^3} (\lambda - U)^{3/2} \left\{ 1 + \frac{(\lambda - U)}{2mc^2} \right\}^{3/2} \quad (\text{V-119})$$



In terms of the dimensionless variables V-59, this becomes

$$\frac{d^2\phi}{d\chi^2} = \frac{\phi^{3/2}}{\chi^{1/2}} \left\{ 1 + \frac{2}{3} \beta(z) \frac{\phi}{\chi} \right\}^{3/2} \quad (V-120)$$

where

$$\beta(z) \equiv \left( \frac{6}{\pi^2} \right)^{1/3} z^4 \frac{e^4}{\hbar^2 c^2} \quad (V-121)$$

To lowest order in  $\beta$ , we therefore have

$$\frac{d^2\phi}{d\chi^2} \approx \frac{\phi^{3/2}}{\chi^{1/2}} \left[ 1 + \beta(z) \frac{\phi}{\chi} \right] \quad (V-122)$$

which gives the desired relativistic piece of V-III.

The model V-119 was first obtained by Vallarta and Rosen (80) but was generally rejected because the resulting density is not normalizable, going as  $r^{-3}$  for small  $r$ , a difficulty which does not persist in V-122. This rejection, we feel, is poorly founded because it is based on too literal an interpretation of the model at extremely small distances from the nucleus. The relativistic correction becomes significant at  $\chi \approx \beta$ , which at  $Z = 92$  is  $\chi \sim .02$ . For this case, the number of electrons contained in a sphere of radius .02 (as given by the uncorrected TF model) is about 2, clearly too few to treat statistically. Furthermore, since V-120 contains  $\beta$  to all orders, it should certainly not be taken literally due to the neglect of higher order  $\beta$  terms (i.e. higher order in  $v/c$ ) in deriving V-112. It is therefore felt that the expanded form V-122, which as we just noted does not have convergence difficulties, can be confidently used.

There is, however, one reservation which must be resolved before the foregoing result can be considered definitive. Comparing V-119 with V-9,

we note that Gilvarry's equation differs from ours in the term  $(er \frac{d\phi}{dr})^2$  which, incidentally, removes the convergence difficulty just cited. The origin of this term is Rudkjøbing's (58) analysis of the Dirac equation and presumably represents a spin-orbit interaction effect. If this is the case, it is difficult to understand why the electron magnetic moment and thus  $\hbar$  does not appear in front of this term. The way to settle the question is clear: the relativistic analog of the first quantum Vlasov equation must be calculated starting from the Pauli equation rather than the Schroedinger equation and its classical limit taken in precisely the same fashion as before. Attention need only be focused on the spin-orbit terms in the Pauli Hamiltonian since it is readily verified that the Kinetic and potential energy terms give exactly V-114. We have not as yet carried out this relatively straightforward program.

The correlation correction, even in lowest order, cannot be obtained so simply in spite of the fact that the formal procedure for obtaining it is well defined. What one must do is to go to the third stage of approximation (see II-85) in the quantum BBGKY hierarchy and thus deal with the coupled equations for  $\tilde{F}^{(2)}$  and  $\tilde{F}^{(1)}$ . In principle, one then solves for  $\tilde{F}^{(2)}$  in terms of  $\tilde{F}^{(1)}$  and computes the right-hand side of II-77. The classical limit of the resulting  $\tilde{F}^{(1)}$  equation is then taken and solved by assuming that the new  $\tilde{F}^{(1)}$  only slightly differs from its uncorrected (or TF) value. In carrying this program out, recourse to an expansion in some small dimensionless parameter will certainly be required. It is therefore advisable to introduce at the outset the dimensionless variables appropriate to the TF model.

Without actually going through this procedure, we can anticipate some general features of the result. The problem will become formally similar to that of obtaining the doublet distribution function in a classical inhomogeneous

plasma whose singlet function in the absence of correlations is the Fermi distribution. Quantum effects will, however, persist in the "classical" limit  $\hbar \rightarrow 0$  in two guises. First, the collision integral (i.e. the right-hand side of II-77) will be modified by the usual  $\left[1 - \frac{Nk^2}{2m^3} \tilde{F}^{(1)}\right]$  factors characteristic of the exclusion principle\* and demanded, in fact, if the collision integral is to be in accord with the H theorem appropriate to Fermi statistics. Second, factors like the  $N/N-1$  term which arose in Section IV-A as a consequence of the Hartree-Fock approximation will generate corrections to  $\tilde{F}^{(2)}$  of the form  $\frac{1}{N} \tilde{F}^{(1)} \tilde{F}^{(1)}$ . Indeed, an unpublished study of the problem by the author and von Roos (81) indicated the possibility that the Fermi-Amaldi correction, which, it may be recalled, was removed by the Hartree-Fock approximation, is to some extent put back by correlations in accord with a similar observation by Jensen (53). Care must therefore be taken\*\* to keep track of terms of order  $1/N$ , a point which appears to have been disregarded in the field-theoretic studies (69, 70) of the correlation question cited earlier.

This formal equivalence between the introduction of correlations into the TF model and what is essentially a problem in classical plasma physics is a cause for some despair since the problem of correlations in a classical inhomogeneous plasma is still unsolved (25,82). It will therefore most likely be necessary to introduce a further simplification, viz., that of disregarding the inhomogeneity of the plasma in the computation of  $F^{(2)}$ . Since the overall effect on the model of the correlation correction is likely to be small, this procedure, which preserves the main physical features of the correlation corrections to  $\tilde{F}^{(2)}$ , is surely adequate. For

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\*Since  $\tilde{F}^{(1)}$  is of order  $\hbar^{-3}$ , it is seen that this term would persist when  $\hbar \rightarrow 0$ .

\*\*In this regard, it should perhaps be mentioned that the normalization constants C' and C'' occurring in II-84 have been evaluated by the method of Section IV-A and found to be  $N/(N-2)$ .



this reason, the results of the next chapter where we actually compute the correlation corrections to  $\tilde{F}^{(2)}$  in an infinite spatially homogeneous electron gas should greatly facilitate the removal of this final barrier to a unified statistical model of the atom.

## Chapter VI    Correlations and Collisions in the Uniform Electron Gas

### A. Introduction

The spatially homogeneous electron gas with a uniformly smeared out background of immobile neutralizing positive charge is a commonly used idealization of the conduction electrons in a metal and has thus received extensive theoretical attention.\* Although most practical problems require the inclusion of the lattice degrees of freedom (i.e. the phonon field) as well, it is clear that a detailed theory of the electron gas itself is a necessary prerequisite to an understanding of the more complete problem.

Due to the formal similarity of the Fermi sphere and the "vacuum" of field theory, the zero-temperature electron gas has been a particularly fertile ground for the application of field-theoretic techniques. However, due to the fact that the "coupling constant" of the problem is the parameter  $r_s$  defined in IV-115 which for metals lies in the range 2-5, we have, in effect, an intermediate to strong coupling problem. Consequently, the field-theoretic approaches which are in essence based on a perturbation expansion in  $r_s$  are of value only in what may be called the "academic" limit  $r_s \ll 1$ . Indeed, since the shielding of the bare Coulomb interaction by the dielectric behaviour of the electron gas is a dominant feature of the problem, one must in effect sum part of the perturbation series to all orders in  $r_s$  to retrieve even the simplest physical processes. In the Gell-Mann-Brueckner (54) calculation of the "correlation energy" of the

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\*A fairly comprehensive survey of this aspect of the many-body problem may be found in Pines (83).

electron gas (i.e. the true ground state energy minus that obtained in the Hartree-Fock approximation) for example, formally divergent contributions from all orders of perturbation theory must be summed to yield the (finite) leading contributions for small  $V_s$ .

In view of the manifest inadequacy of perturbation theory at realistic densities, attention has been focused on what may be termed "non-perturbative" approaches. An early example is the elegant formalism of Nozières and Pines (32) wherein the ground state energy and pair correlation function are related on general grounds to the dielectric constant of the system. When the dielectric constant as computed in the Hartree approximation (i.e. III-42) is fed into their expression, one obtains the result of Gell-Mann-Brueckner, neglecting, however, the exchange contributions. This neglect of exchange is unfortunately a serious drawback since at metallic densities the exchange interaction is expected to play a significant role. The method nevertheless has value inasmuch as an improved calculation of the dielectric constant may be an easier task than a direct energy calculation.\*

Another non-perturbative approach has recently been used by von Roos (34) to calculate the effect of correlations on the dielectric constant. In analogy to the first Tamm-Dancoff approximation in meson theory, he retains all intermediate states which contain a single-particle hole pair, neglecting all others. Use of second quantization obviates exchange difficulties. His results for the shift in the zero of the dielectric constant (i.e. the plasmon energy) are in encouraging agreement with experimental results at metallic densities indicating the possible viability of the

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\*One might expect, for example, that use of the Hartree-Fock dielectric constant as obtained from IV-89 would mitigate the exchange difficulty to some extent.



method, perhaps in conjunction with the Nozieres-Pines formalism, for the computation of other details of the system.

In Chapters III and IV, we have already studied the electron gas in the Hartree and Hartree-Fock approximation. We now go beyond Hartree-Fock to the third stage of approximation in the quantum BBGKY hierarchy as outlined in Chapter II. In so doing, we are in effect introducing another non-perturbative approach to the problem with the unique property, however, of being phrased entirely in classical terms. Furthermore, since we proceed from the Hartree-Fock approximation, the effect of correlations on the exchange interaction is automatically included at least to "lowest order". The quotation marks underscore a drawback which our method shares with all non-perturbative approaches. Unlike perturbation theory where bounds can at least be set on the next term in the series (notwithstanding the fact that knowledge of the next term in a slowly convergent series is of somewhat dubious value), we have as yet found no way of even estimating how our results would be altered in the fourth and higher stages of approximation. All we can offer is the qualitative consideration that if correlations between more than two particles are an important feature of the problem, the system is more characteristic of a liquid than a gas and entirely different techniques must be applied.

With this reservation in mind, we proceed in Section B to the third stage of approximation to the quantum BBGKY hierarchy and derive an equation relating the "correlation functions" (i.e.  $\tilde{F}_{\alpha, \alpha_2}^{(2)} - (\tilde{F}_{\alpha, \alpha_2}^{(2)})_{\text{Hartree-Fock}}$ ) to  $\tilde{F}^{(1)}$ . In so doing, we directly parallel a recent study by Guernsey (18) which, being based on the Wigner q.m.d.f., does not properly include exchange. Indeed, we obtain Guernsey's result plus an additional term which describes the correlation modification of the exchange interaction. Fortunately, the

resultant singular integral equation for the correlation function still belongs to the general class of equations solved by Guernsey in an earlier paper (25), thereby enabling us to make direct use of his result with a consequent saving of labor. Due to this circumstance, his contribution to the present problem cannot be minimized, notwithstanding the fact that the integral equation in question is apparently of a fairly standard type.

Having obtained the correlation function expressed in terms of  $\tilde{F}^{(0)}$ , in Section C we introduce it into the  $\tilde{F}^{(1)}$  equation to obtain the "collision integral". The vanishing of the collision integral is a necessary condition on  $\tilde{F}^{(1)}$  if it is to represent a system in equilibrium. The modifications of the collision integral wrought by exchange (which we believe to be a new result) may, due to the added complexity of the total expression, lead to equilibrium  $\tilde{F}^{(0)}$ 's other than the Fermi distribution. We neglect this possibility, however, in Section D where we compute the correlation energy at zero temperature, assuming  $\tilde{F}^{(0)}$  to be the Fermi sphere. The equivalence of our result with that of Gell-Mann and Brueckner (GB) is explicitly demonstrated in the high density limit ( $r_s \ll 1$ ) by means of an analytic continuation similar to that used by Sawada et al (85). We then go beyond the GB result to compute the exchange contribution to the  $r_s \log r_s$  term in the energy, which arises from the screening of the exchange interaction by the dielectric behaviour of the system.

## B. Solution for the Pair Correlation Function

The basic equations of the theory are the time-independent\* forms of II-79 and II-81 which, for the problem at hand, become

$$\frac{iNg^2}{\hbar(2\pi)^3} \sum_{\alpha_2=\pm 1/2}^{+1/2} \int d^3x_2 d^3v_2 d^3q e^{i\mathbf{q}\cdot(\mathbf{x}_1-\mathbf{x}_2)} f(\mathbf{q}) \left[ \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2) - \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) \right] \equiv \frac{\partial \tilde{F}_{\alpha_1}^{(1)}}{\partial t} \Big|_{\text{Collisions}} = 0 \quad (\alpha_1 = \pm 1/2) \quad (\text{VI-1})$$

(where use has been made of the spatial homogeneity of  $\tilde{F}^{(1)}$ ) and

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\*The time-independent equations are used because the system is assumed to be in equilibrium. In the third stage of approximation, however, we are actually developing a kinetic theory of an isolated system rather than a statistical description of an ensemble as discussed in Chapter II. It is therefore necessary to introduce the concept of equilibrium in a dynamical sense by formally considering the time dependent quantum BBGKY hierarchy, viewed as an initial value problem, and defining equilibrium in terms of the asymptotic values of the  $\tilde{F}^{(s)}$  as  $t \rightarrow \infty$ . This procedure, which introduces irreversibility into the otherwise reversible theory, has been extensively discussed in the literature (25,28,82), so we will not burden the present development with such considerations. Instead, we will follow the conventional practice of dealing with the time-independent equations, with the understanding that ambiguities in the interpretation of dynamical singularities in the solution for  $\tilde{F}^{(2)}$  are to be resolved from its time dependent equation by imagining it to be multiplied by  $e^{\epsilon t}$  where  $\epsilon$  is a positive infinitesimal. This can be viewed either as a causality requirement in the initial value problem approach or as Bogoliubov's (6) condition that all correlations must vanish in the infinite past. The net result of this procedure are the factors of  $i\epsilon$  in VI-20 et seq. Finally, it should be noted that for time dependent processes in which  $\tilde{F}^{(1)}$  varies at a rate slow compared to the characteristic relaxation time of  $\tilde{F}^{(2)}$  (i.e. the hydrodynamic limit), we can assume that  $\tilde{F}^{(2)}$  depends on time only implicitly via its dependence on  $\tilde{F}^{(1)}$  and thus that the solution for  $\tilde{F}^{(2)}$  obtained from the time-independent equations is still valid.



$$\begin{aligned}
 & \left( \underline{v}_1 \cdot \nabla_{\underline{x}_1} + \underline{v}_2 \cdot \nabla_{\underline{x}_2} - \frac{i\hbar}{2m} \nabla_{\underline{x}_1}^2 - \frac{i\hbar}{2m} \nabla_{\underline{x}_2}^2 \right) \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \\
 & \frac{ig^2}{\hbar(2\pi)^3} \int d^3q e^{i\underline{q} \cdot (\underline{x}_1 - \underline{x}_2)} f(\underline{q}) \left[ \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1 + \frac{\hbar}{m}\underline{q}, \underline{v}_2 - \frac{\hbar}{m}\underline{q}) - \tilde{F}_{\alpha_1, \alpha_2}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right] \\
 & + \frac{iNg^2}{\hbar(2\pi)^3} \sum_{\alpha_3 = -1/2}^{1/2} \int d^3x_3 d^3v_3 d^3q f(\underline{q}) \left\{ e^{i\underline{q} \cdot (\underline{x}_1 - \underline{x}_3)} \left[ \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1 + \frac{\hbar}{m}\underline{q}, \underline{v}_2, \underline{v}_3) \right. \right. \\
 & - \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) \left. \right] + e^{i\underline{q} \cdot (\underline{x}_2 - \underline{x}_3)} \left[ \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2 + \frac{\hbar}{m}\underline{q}, \underline{v}_3) \right. \\
 & \left. \left. - \tilde{F}_{\alpha_1, \alpha_2, \alpha_3}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) \right] \right\} \quad (\alpha_1, \alpha_2 = -1/2, 1/2)
 \end{aligned}$$

(VI-2)

$f(\underline{q})$  and  $g^2$  are given by their Coulomb values, III-39, but for the sake of convenience and generality will be kept arbitrary in the ensuing development. Due to the fact that  $N$  is formally infinite, we everywhere ignore the distinction between  $(N-1, N-2, \text{ etc.})$  and  $N$ .

The third stage of approximation to the quantum BBGKY hierarchy is characterized by the following assumptions about  $\tilde{F}^{(2)}$  and  $\tilde{F}^{(3)}$  (see Chapter II):

$$\tilde{F}_{\uparrow\uparrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \left( 1 - e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right) \tilde{F}_{\uparrow}^{(1)}(\underline{v}_1) \tilde{F}_{\uparrow}^{(1)}(\underline{v}_2) + \frac{1}{4} H(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2)$$

(VI-3)

$$\tilde{F}_{\uparrow\downarrow}^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \tilde{F}_{\uparrow}^{(1)}(\underline{v}_1) \tilde{F}_{\downarrow}^{(1)}(\underline{v}_2) + \frac{1}{4} G(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2)$$

(VI-4)

and

$$\begin{aligned} \widetilde{F}_{\uparrow\uparrow\downarrow}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) &= \left[ 1 - e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right] \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_1) \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_2) \widetilde{F}_{\downarrow}^{(1)}(\underline{v}_3) \\ &+ \frac{1}{4} \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_1) G(\underline{x}_2 - \underline{x}_3; \underline{v}_2, \underline{v}_3) + \frac{1}{4} \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_2) G(\underline{x}_1 - \underline{x}_3; \underline{v}_1, \underline{v}_3) + \frac{1}{4} \widetilde{F}_{\downarrow}^{(1)}(\underline{v}_3) H(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2) \end{aligned}$$

$$\begin{aligned} \widetilde{F}_{\uparrow\uparrow\uparrow}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) &= \left[ 1 - e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} - e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_1 - \underline{v}_3) \cdot (\underline{x}_1 - \underline{x}_3)} \right. \\ &- e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} + e^{-\frac{i\mathbf{m}}{\hbar}[(\underline{v}_2 - \underline{v}_1) \cdot \underline{x}_2 + (\underline{v}_3 - \underline{v}_2) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_3) \cdot \underline{x}_1]} \\ &+ e^{-\frac{i\mathbf{m}}{\hbar}[(\underline{v}_3 - \underline{v}_1) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_2) \cdot \underline{x}_1 + (\underline{v}_2 - \underline{v}_3) \cdot \underline{x}_2]} \left. \right] \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_1) \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_2) \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_3) \\ &+ \frac{1}{4} \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_1) H(\underline{x}_2 - \underline{x}_3; \underline{v}_2, \underline{v}_3) + \frac{1}{4} \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_2) H(\underline{x}_1 - \underline{x}_3; \underline{v}_1, \underline{v}_3) \\ &+ \frac{1}{4} \widetilde{F}_{\uparrow}^{(1)}(\underline{v}_3) H(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2) \end{aligned} \quad (VI-5)$$

(VI-6)

etc., where implicit use has again been made of the spatial homogeneity of the system. It is important to note that the anti-parallel and parallel spin "correlation functions", G and H (respectively), which represent the deviation from the Hartree-Fock approximation, do not explicitly embody the requisite exchange symmetry nor is the correlation part of  $\widetilde{F}^{(3)}$  explicitly exchange symmetrized. As pointed out in Chapter II, these symmetrizations take place in the fourth stage of approximation.

We shall restrict our considerations to the "normal" or paramagnetic case defined in IV-63. We therefore define

$$\widetilde{F}_{\uparrow}^{(1)} = \widetilde{F}_{\downarrow}^{(1)} \equiv \frac{1}{2} \widetilde{F}^{(1)} \quad (VI-7)$$

the normalization of  $\widetilde{F}^{(1)}$  being

$$N \int d^3v \widetilde{F}^{(1)}(v) = n \quad (VI-8)$$

where  $n$  is the electron density. Then, summing VI-1 over the spin index and using VI-3 and VI-4 leads to the collision integral

$$\left. \frac{\partial \tilde{F}^{(1)}(v)}{\partial t} \right|_{\text{collisions}} = \frac{iNg^2}{\hbar(2\pi)^3} \int d^3x_2 \int d^3v_2 \int d^3q e^{i\mathbf{q} \cdot (\mathbf{x}_1 - \mathbf{x}_2)} f(\mathbf{q})$$

$$\times \left[ \frac{1}{2} \left( G(\mathbf{x}_1 - \mathbf{x}_2, \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2) + H(\mathbf{x}_1 - \mathbf{x}_2, \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2) \right) - \frac{1}{2} \left( G(\mathbf{x}_1 - \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2) + H(\mathbf{x}_1 - \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2) \right) \right]$$

(VI-9)

We are thus led to consider in place of G and H the more convenient quantities

$$J \equiv \frac{1}{2} [G + H] \quad \text{(VI-10)}$$

and

$$K \equiv \frac{1}{2} [G - H] \quad \text{(VI-11)}$$

The equations for J and K are simply obtained from VI-2 through VI-6.

Thus summation of VI-2 over  $\alpha_1$  and  $\alpha_2$  yields for J:

$$\left( \mathbf{v}_1 \cdot \nabla_{\mathbf{x}_1} + \mathbf{v}_2 \cdot \nabla_{\mathbf{x}_2} - \frac{i\hbar}{2m} \nabla_{\mathbf{x}_1}^2 - \frac{i\hbar}{2m} \nabla_{\mathbf{x}_2}^2 \right) J(\mathbf{x}_1 - \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) = \frac{ig^2}{\hbar(2\pi)^3} \int d^3q e^{i\mathbf{q} \cdot (\mathbf{x}_1 - \mathbf{x}_2)} f(\mathbf{q})$$

$$\times \left\{ \left[ \tilde{F}_0^{(2)}(\mathbf{x}_1, \mathbf{x}_2; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2 - \frac{\hbar}{m}\mathbf{q}) - \tilde{F}_0^{(2)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{v}_1, \mathbf{v}_2) \right] + \left[ J(\mathbf{x}_1 - \mathbf{x}_2; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2 - \frac{\hbar}{m}\mathbf{q}) \right. \right.$$

$$\left. - J(\mathbf{x}_1 - \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) \right\} + \frac{iNg^2}{\hbar(2\pi)^3} \int d^3x_3 \int d^3v_3 \int d^3q f(\mathbf{q}) \left\{ e^{i\mathbf{q} \cdot (\mathbf{x}_1 - \mathbf{x}_3)} \left[ \tilde{F}_0^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2, \mathbf{v}_3) \right. \right.$$

$$\left. - \tilde{F}_0^{(3)}(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3; \mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3) \right] + \left( \tilde{F}^{(1)}(\mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}) - \tilde{F}^{(1)}(\mathbf{v}_1) \right) J(\mathbf{x}_2 - \mathbf{x}_3, \mathbf{v}_2, \mathbf{v}_3)$$

$$+ \left( J(\mathbf{x}_2 - \mathbf{x}_3; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_3) - J(\mathbf{x}_2 - \mathbf{x}_3; \mathbf{v}_1, \mathbf{v}_3) \right) \tilde{F}^{(1)}(\mathbf{v}_2)$$

$$+ \left( J(\mathbf{x}_1 - \mathbf{x}_2; \mathbf{v}_1 + \frac{\hbar}{m}\mathbf{q}, \mathbf{v}_2) - J(\mathbf{x}_1 - \mathbf{x}_2; \mathbf{v}_1, \mathbf{v}_2) \right) \tilde{F}^{(1)}(\mathbf{v}_3) \left. \right\} + \{1 \leftrightarrow 2\}$$



where the spin-summed (uncorrelated) quantities  $\tilde{F}_0^{(2)}$  and  $\tilde{F}_0^{(3)}$  are defined by

$$\tilde{F}_0^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) - \frac{1}{2} e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \quad (\text{VI-13})$$

and

$$\begin{aligned} \tilde{F}_0^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) &= \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \tilde{F}^{(1)}(\underline{v}_3) - \frac{1}{2} \left[ e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \right. \\ &+ e^{-\frac{i m}{\hbar}(\underline{v}_1 - \underline{v}_3) \cdot (\underline{x}_1 - \underline{x}_3)} + e^{-\frac{i m}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} \left. \right] \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \tilde{F}^{(1)}(\underline{v}_3) \\ &+ \frac{1}{4} \left[ e^{-\frac{i m}{\hbar}[(\underline{v}_2 - \underline{v}_1) \cdot \underline{x}_2 + (\underline{v}_3 - \underline{v}_2) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_3) \cdot \underline{x}_1]} + e^{-\frac{i m}{\hbar}[(\underline{v}_3 - \underline{v}_1) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_2) \cdot \underline{x}_1 + (\underline{v}_2 - \underline{v}_3) \cdot \underline{x}_2]} \right] \\ &\times \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \tilde{F}^{(1)}(\underline{v}_3) \end{aligned} \quad (\text{VI-14})$$

Similarly, the K equation is obtained by deriving from VI-2 the equation for  $(\tilde{F}_{\uparrow\uparrow}^{(2)} + \tilde{F}_{\downarrow\downarrow}^{(2)} - \tilde{F}_{\uparrow\downarrow}^{(2)} - \tilde{F}_{\downarrow\uparrow}^{(2)})$ . The result is

$$\begin{aligned} &\left[ \underline{v}_1 \cdot \nabla_{\underline{x}_1} + \underline{v}_2 \cdot \nabla_{\underline{x}_2} - \frac{i \hbar}{2m} \nabla_{\underline{x}_1}^2 - \frac{i \hbar}{2m} \nabla_{\underline{x}_2}^2 \right] K(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) = \frac{ig^2}{\hbar(2\pi)^3} \int d^3 \underline{q} e^{i \underline{q} \cdot (\underline{x}_1 - \underline{x}_2)} f(\underline{q}) \\ &\times \left\{ \left[ A^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1 + \frac{\hbar}{m} \underline{q}, \underline{v}_2 - \frac{\hbar}{m} \underline{q}) - A^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right] \right. \\ &\quad \left. + \left[ K(\underline{x}_1, \underline{x}_2, \underline{v}_1 + \frac{\hbar}{m} \underline{q}, \underline{v}_2 - \frac{\hbar}{m} \underline{q}) - K(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right] \right\} \\ &+ \frac{iNg^2}{\hbar(2\pi)^3} \int d^3 \underline{x}_3 d^3 \underline{v}_3 d^3 \underline{q} f(\underline{q}) \left\{ e^{i \underline{q} \cdot (\underline{x}_1 - \underline{x}_3)} \left[ \left( B_{12}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1 + \frac{\hbar}{m} \underline{q}, \underline{v}_2, \underline{v}_3) \right. \right. \right. \\ &\quad \left. \left. - B_{12}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) \right) + \left( K(\underline{x}_1, \underline{x}_2; \underline{v}_1 + \frac{\hbar}{m} \underline{q}, \underline{v}_2) \right. \right. \\ &\quad \left. \left. - K(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \right) \tilde{F}^{(1)}(\underline{v}_3) \right] + \{1 \leftrightarrow 2\} \left. \right\} \end{aligned} \quad (\text{VI-15})$$

where

$$A^{(2)}(\underline{x}_1, \underline{x}_2; \underline{v}_1, \underline{v}_2) \equiv \frac{1}{2} e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \quad (\text{VI-16})$$

and

$$\begin{aligned} B_{12}^{(3)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) &= B_{21}^{(3)}(\underline{x}_2, \underline{x}_1, \underline{x}_3; \underline{v}_2, \underline{v}_1, \underline{v}_3) \equiv \frac{1}{2} e^{-\frac{im}{\hbar}(\underline{v}_1 - \underline{v}_2) \cdot (\underline{x}_1 - \underline{x}_2)} \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \tilde{F}^{(1)}(\underline{v}_3) \\ &- \frac{1}{4} \left[ e^{-\frac{im}{\hbar}[(\underline{v}_2 - \underline{v}_1) \cdot \underline{x}_2 + (\underline{v}_3 - \underline{v}_2) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_3) \cdot \underline{x}_1]} \right. \\ &\quad \left. + e^{-\frac{im}{\hbar}[(\underline{v}_3 - \underline{v}_1) \cdot \underline{x}_3 + (\underline{v}_1 - \underline{v}_2) \cdot \underline{x}_1 + (\underline{v}_2 - \underline{v}_3) \cdot \underline{x}_2]} \right] \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \tilde{F}^{(1)}(\underline{v}_3) \end{aligned} \quad (\text{VI-17})$$

Equations VI-12 and VI-15 are most conveniently attacked by introducing the Fourier transforms:

$$J(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2) \equiv \int d^3k e^{i\mathbf{k} \cdot (\underline{x}_2 - \underline{x}_1)} f(\mathbf{k}, \underline{v}_1, \underline{v}_2) \quad (\text{VI-18})$$

and

$$K(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2) \equiv \int d^3k e^{i\mathbf{k} \cdot (\underline{x}_2 - \underline{x}_1)} \chi(\mathbf{k}, \underline{v}_1, \underline{v}_2) \quad (\text{VI-19})$$

in terms of which the left-hand side of VI-12 becomes

$$\frac{im}{\hbar} \int d^3k e^{i\mathbf{k} \cdot (\underline{x}_2 - \underline{x}_1)} \left\{ \left[ (\underline{v}_2 - \underline{v}_1 + \frac{\hbar}{m} \mathbf{k}) \cdot \frac{\hbar}{m} \mathbf{k} - i\epsilon \right] f(\mathbf{k}, \underline{v}_1, \underline{v}_2) \right\} \quad (\text{VI-20})$$

(a precisely similar result naturally is obtained for the l.h.s. of VI-15) where  $\epsilon$  is a positive infinitesimal whose origin is discussed in the footnote on page 158.

The consequent reductions of the right-hand sides of VI-12 and VI-15 are perfectly straightforward though sufficiently lengthy to render unprofitable an exhibition of the details. We shall therefore just quote the

resulting equations for  $\mathcal{G}$  and  $\mathcal{K}$ . We find

$$\begin{aligned}
 m \left[ (\underline{v}_2 - \underline{v}_1 + \frac{\hbar}{m} \underline{k}) \cdot \frac{\hbar}{m} \underline{k} - i\epsilon \right] \mathcal{G}(\underline{k}, \underline{v}_1, \underline{v}_2) &= N g^2 f(\underline{k}) \left[ \tilde{F}^{(1)}(\underline{v}_1 - \frac{\hbar}{m} \underline{k}) - \tilde{F}^{(1)}(\underline{v}_1) \right] \\
 \times \int d^3 v' \mathcal{G}(\underline{k}, \underline{v}', \underline{v}_2) &+ N g^2 f(\underline{k}) \left[ \tilde{F}^{(1)}(\underline{v}_2 + \frac{\hbar}{m} \underline{k}) - \tilde{F}^{(1)}(\underline{v}_2) \right] \int d^3 v' \mathcal{G}(\underline{k}, \underline{v}_1, \underline{v}') \\
 + \left[ S(\underline{k}, \underline{v}_1, \underline{v}_2) - \frac{1}{2} S\left(\frac{m}{\hbar}(\underline{v}_1 - \underline{v}_2) - \underline{k}, \underline{v}_1, \underline{v}_2\right) \right] \\
 + \left\{ \frac{1}{(2\pi)^3} g^2 \int d^3 q f(q) \left[ \mathcal{G}(\underline{k} - \underline{q}, \underline{v}_1 - \frac{\hbar}{m} \underline{q}, \underline{v}_2 + \frac{\hbar}{m} \underline{q}) - \mathcal{G}(\underline{k} - \underline{q}, \underline{v}_1, \underline{v}_2) \right] \right\}
 \end{aligned}
 \tag{VI-21}$$

where

$$\begin{aligned}
 S(\underline{k}, \underline{v}_1, \underline{v}_2) &\equiv \frac{g^2 f(\underline{k})}{(2\pi)^3} \left[ \tilde{F}^{(1)}(\underline{v}_1 - \frac{\hbar}{m} \underline{k}) \tilde{F}^{(1)}(\underline{v}_2 + \frac{\hbar}{m} \underline{k}) \left[ 1 - \frac{N \hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1) \right] \left[ 1 - \frac{N \hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2) \right] \right. \\
 &\quad \left. - \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \left[ 1 - \frac{N \hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1 - \frac{\hbar}{m} \underline{k}) \right] \left[ 1 - \frac{N \hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2 + \frac{\hbar}{m} \underline{k}) \right] \right]
 \end{aligned}
 \tag{VI-22}$$

Similarly, for  $\mathcal{K}$  we obtain simply

$$\begin{aligned}
 m \left[ (\underline{v}_2 - \underline{v}_1 + \frac{\hbar}{m} \underline{k}) \cdot \frac{\hbar}{m} \underline{k} - i\epsilon \right] \mathcal{K}(\underline{k}, \underline{v}_1, \underline{v}_2) &= \frac{1}{2} S\left(\frac{m}{\hbar}(\underline{v}_1 - \underline{v}_2) - \underline{k}, \underline{v}_1, \underline{v}_2\right) \\
 + \left\{ \frac{1}{(2\pi)^3} g^2 \int d^3 q f(q) \left[ \mathcal{K}(\underline{k} - \underline{q}, \underline{v}_1 - \frac{\hbar}{m} \underline{q}, \underline{v}_2 + \frac{\hbar}{m} \underline{q}) - \mathcal{K}(\underline{k} - \underline{q}, \underline{v}_1, \underline{v}_2) \right] \right\}
 \end{aligned}
 \tag{VI-23}$$

We now focus attention on the curly-bracketed terms in VI-21 and VI-23 which, it will be noted, drastically complicate these equations. They originate from the correlation corrections to the first terms on the right-hand side of VI-12 and VI-15. Since the uncorrected contributions to these terms



(i.e. those arising from  $\tilde{F}_0^{(2)}$  in VI-12 and  $A^{(2)}$  in VI-15) are non-vanishing, one would suspect that the troublesome terms in some sense represent higher-order corrections and hence can be ignored. Indeed, by inserting a formal expansion parameter (eventually set equal to unity) in the quantum BBGKY hierarchy, Guernsey (18) has shown that these terms do not appear in lowest order. While we could, of course, have followed the same somewhat arbitrary procedure, we choose instead to argue these terms away by demonstrating that they are of the same form and magnitude as those additional terms which enter in the fourth stage of approximation to the BBGKY hierarchy.

To illustrate this, let us first choose a typical  $\tilde{F}^{(3)}$ , say  $\tilde{F}_{\downarrow\uparrow\uparrow}^{(3)}$ , and see what modifications of the appropriate ansatz VI-5 would be required in the fourth stage of approximation. It is readily verified that the exchange symmetry requirements II-70 and II-72 are satisfied if

$$\begin{aligned} \tilde{F}_{\downarrow\uparrow\uparrow}^{(4)}(\underline{x}_1, \underline{x}_2, \underline{x}_3; \underline{v}_1, \underline{v}_2, \underline{v}_3) = & \left[ 1 - e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} \right] \tilde{F}_{\downarrow}^{(4)}(\underline{v}_1) \tilde{F}_{\uparrow}^{(4)}(\underline{v}_2) \tilde{F}_{\uparrow}^{(4)}(\underline{v}_3) \\ & + \frac{1}{4} \tilde{F}_{\uparrow}^{(4)}(\underline{v}_2) G(\underline{x}_1 - \underline{x}_3; \underline{v}_1, \underline{v}_3) + \frac{1}{4} \tilde{F}_{\uparrow}^{(4)}(\underline{v}_3) G(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_2) \\ & + \frac{1}{4} \tilde{F}_{\downarrow}^{(4)}(\underline{v}_1) H(\underline{x}_2 - \underline{x}_3; \underline{v}_2, \underline{v}_3) - \left\{ \frac{1}{4} e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} \left[ H(\underline{x}_3 - \underline{x}_2; \underline{v}_2, \underline{v}_3) \tilde{F}_{\downarrow}^{(4)}(\underline{v}_1) \right. \right. \\ & \left. \left. + G(\underline{x}_1 - \underline{x}_2; \underline{v}_1, \underline{v}_3) \tilde{F}_{\uparrow}^{(4)}(\underline{v}_2) + G(\underline{x}_1 - \underline{x}_3; \underline{v}_1, \underline{v}_2) \tilde{F}_{\uparrow}^{(4)}(\underline{v}_3) \right] \right\} \quad (\text{VI-24}) \end{aligned}$$

where the term in curly brackets represents the new contribution. Inserting it into VI-2, we would obtain, among others, an additional term of the form

$$\begin{aligned} & \frac{-iNg^2}{\hbar(2\pi)^3} \int d^3x_3 d^3v_3 d^3q f(q) e^{i\mathbf{q} \cdot (\underline{x}_1 - \underline{x}_3)} \cdot \frac{1}{8} \cdot e^{-\frac{i\mathbf{m}}{\hbar}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} \tilde{F}_{\uparrow}^{(4)}(\underline{v}_3) \\ & \times \left[ G(\underline{x}_1 - \underline{x}_3; \underline{v}_1 + \frac{\hbar}{m}\mathbf{q}, \underline{v}_2) - G(\underline{x}_1 - \underline{x}_3; \underline{v}_1, \underline{v}_2) \right] \end{aligned}$$

(VI-25)

or, in terms of the Fourier transform,  $(\mathcal{F})$ , of  $G$

$$\begin{aligned} & -\frac{iNg^2}{h(2\pi)^3} \cdot \frac{1}{8} \int d^3x_3 d^3v_3 d^3q d^3k f(q) e^{iq \cdot (\underline{x}_1 - \underline{x}_3)} e^{-\frac{im}{h}(\underline{v}_2 - \underline{v}_3) \cdot (\underline{x}_2 - \underline{x}_3)} e^{ik \cdot (\underline{x}_3 - \underline{x}_1)} \\ & \times \widetilde{F}^{(1)}(v_3) \left[ \mathcal{G}(k, \underline{v}_1 + \frac{k}{m}, \underline{v}_2) - \mathcal{G}(k, \underline{v}_1, \underline{v}_2) \right] \end{aligned} \quad (\text{VI-26})$$

Performing the integrals over  $\underline{x}_3$  and  $\underline{v}_3$ , we find after a few manipulations that VI-26 can be written as

$$\begin{aligned} & -\frac{iNg^2h^3}{h^3 8m^3} \int d^3k e^{ik \cdot (\underline{x}_2 - \underline{x}_1)} \left[ \widetilde{F}^{(1)}(\underline{v}_2 + \frac{k}{m}) \int d^3q f(q) \left( \mathcal{G}(k-q, \underline{v}_1 - \frac{k}{m}, \underline{v}_2) \right. \right. \\ & \quad \left. \left. - \mathcal{G}(k-q, \underline{v}_1, \underline{v}_2) \right) \right] \end{aligned} \quad (\text{VI-27})$$

As a result, a term would be added to VI-21 of the form

$$-\frac{g^2}{4(2\pi)^3} \left[ \frac{Nh^3}{2m^3} \widetilde{F}^{(1)}(\underline{v}_2 + \frac{k}{m}) \right] \int d^3q f(q) \left( \mathcal{G}(k-q, \underline{v}_1 - \frac{k}{m}, \underline{v}_2) - \mathcal{G}(k-q, \underline{v}_1, \underline{v}_2) \right) \quad (\text{VI-28})$$

Since  $\frac{Nh^3}{2m^3} \widetilde{F}^{(1)}$  is of order unity, it is clear that VI-28 is of the same magnitude and similar structure as the last term of VI-21, which we set out to demonstrate.

Having disposed of the troublesome terms, VI-23 is immediately solved to yield

$$\chi(\underline{k}, \underline{v}_1, \underline{v}_2) = \frac{1}{2m} \frac{S(\frac{m}{h}(\underline{v}_1 - \underline{v}_2) - \underline{k}, \underline{v}_1, \underline{v}_2)}{[(\underline{v}_2 - \underline{v}_1 + \frac{k}{m}) \cdot \frac{k}{m} - i\epsilon]} \quad (\text{VI-29})$$

Turning to VI-21 (minus the last term) we make the convenient variable change

$$\frac{k}{m} \underline{k} \equiv \underline{q} \quad (\text{VI-30})$$

and write this equation as

$$\begin{aligned}
 J(\underline{q}, \underline{v}_1, \underline{v}_2) = & \frac{Ng^2 f(\frac{m}{k}q) [\tilde{F}^{(1)}(\underline{v}_1 - \underline{q}) - \tilde{F}^{(1)}(\underline{v}_1)]}{m [(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon]} \int d^3 v' J(\underline{q}, \underline{v}', \underline{v}_2) \\
 & + \frac{Ng^2 f(\frac{m}{k}q) [\tilde{F}^{(1)}(\underline{v}_2 + \underline{q}) - \tilde{F}^{(1)}(\underline{v}_2)]}{m [(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon]} \int d^3 v' J(\underline{q}, \underline{v}_1, \underline{v}') \\
 & + \frac{[S'(\underline{q}, \underline{v}_1, \underline{v}_2) - \frac{1}{2} S'(\underline{v}_1 - \underline{v}_2 - \underline{q}, \underline{v}_1, \underline{v}_2)]}{[(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon]}
 \end{aligned}
 \tag{VI-31}$$

where

$$f(x) = \frac{4\pi}{x^2} \qquad g^2 = e^2
 \tag{VI-32}$$

and

$$\begin{aligned}
 S'(\underline{q}, \underline{v}_1, \underline{v}_2) = & \frac{g^2 f(\frac{m}{k}q)}{m (2\pi)^3} \left\{ \tilde{F}^{(1)}(\underline{v}_1 - \underline{q}) \tilde{F}^{(1)}(\underline{v}_2 + \underline{q}) \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1) \right] \right. \\
 & \times \left. \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2) \right] - \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1 - \underline{q}) \right] \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2 + \underline{q}) \right] \right\}
 \end{aligned}
 \tag{VI-33}$$

Integrating VI-31 over  $\underline{v}_2$ , and making use of the obvious symmetry

$$J(\underline{q}, \underline{v}', \underline{v}_2) = J(-\underline{q}, \underline{v}_2, \underline{v}')
 \tag{VI-34}$$

we obtain the equation

$$\begin{aligned}
 & \left[ 1 - \int d^3 v_2 \frac{D(-\underline{q}, \underline{v}_2)}{(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon} \right] P(\underline{q}, \underline{v}_1) - D(\underline{q}, \underline{v}_1) \int d^3 v_2 \frac{P(-\underline{q}, \underline{v}_2)}{(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon} \\
 & = Q(\underline{q}, \underline{v}_1)
 \end{aligned}
 \tag{VI-35}$$



where

$$P(\underline{q}, \underline{v}) = \int d^3 v_2 \, f(\underline{q}, \underline{v}_1, \underline{v}_2) \quad (\text{VI-36})$$

$$D(\underline{q}, \underline{v}) = \frac{N}{m} q^2 f\left(\frac{m}{\hbar} q\right) \left[ \tilde{F}^{(1)}(\underline{v} - \underline{q}) - \tilde{F}^{(1)}(\underline{v}) \right] \quad (\text{VI-37})$$

and

$$Q(\underline{q}, \underline{v}) = \frac{\int d^3 v_2 \left[ S'(\underline{q}, \underline{v}_1, \underline{v}_2) - \frac{1}{2} S'(\underline{v}_1 - \underline{v}_2 - \underline{q}, \underline{v}_1, \underline{v}_2) \right]}{[(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon]} \quad (\text{VI-38})$$

From VI-37 and the fact that

$$\tilde{F}^{(1)}(\underline{u}) = \tilde{F}^{(1)}(|\underline{u}|) \quad (\text{VI-39})$$

one finds

$$D(-\underline{q}, \underline{v}) = D(\underline{q}, -\underline{v}) \quad (\text{VI-40})$$

so that VI-35 becomes finally

$$\begin{aligned} & \left[ 1 + \int d^3 v_2 \frac{D(\underline{q}, \underline{v}_2)}{(\underline{v}_2 + \underline{v}_1 - \underline{q}) \cdot \underline{q} + i\epsilon} \right] P(\underline{q}, \underline{v}) - D(\underline{q}, \underline{v}) \int d^3 v_2 \frac{P(-\underline{q}, \underline{v}_2)}{(\underline{v}_2 - \underline{v}_1 + \underline{q}) \cdot \underline{q} - i\epsilon} \\ & = Q(\underline{q}, \underline{v}) \end{aligned} \quad (\text{VI-41})$$

At this point we compare VI-41 with the corresponding equation obtained by Guernsey from the quantum BBGKY hierarchy for the Wigner q.m.d.f. After making the proper notational transformations, we find that it differs from our equation only in that in place of VI-38 he obtains

$$Q_{\text{GUERNSEY}}(\underline{q}, \underline{v}) = \frac{\int d^3 v_2 S'(\underline{q}, \underline{v}, \underline{v}_2)}{[(\underline{v}_2 - \underline{v} + \underline{q}) \cdot \underline{q} - i\epsilon]} \quad (\text{VI-42})$$

and thus ignores the exchange contribution to  $Q$ . It is worth noting, however, that he included enough of exchange to obtain the  $\left[1 - \frac{N h^3}{2 m^3} \tilde{F}^{(0)}\right]$  factors in VI-33 which are characteristic of the exclusion principle.

Equation VI-41 has been solved for general  $Q$  by Guernsey in earlier paper (25). The method consists of first integrating it over the components of  $\underline{v}$  normal to  $\underline{q}$  to obtain a one dimensional equation. The introduction of Hilbert transforms then reduces it a form amenable to standard techniques from the theory of singular integral equations.

Introducing the notation\*

$$\Delta(\underline{q}, \underline{\Omega}) \equiv 1 + \frac{\int d^3 v' \frac{D(\underline{q}, \underline{v}')}{\underline{\Omega} + \underline{q} \cdot (\underline{v}' - \underline{q}) + i\epsilon}}{\quad} \quad (\text{VI-43})$$

we find from equation 61 of reference (25) that (in our notation)

$$P(\underline{q}, \underline{v}) = \frac{Q(\underline{q}, \underline{v})}{\Delta(\underline{q}, \underline{v}, \underline{q})} + D(\underline{q}, \underline{v}) \int_{-\infty}^{\infty} du \frac{\phi(\underline{q}, u)}{[(u - \underline{v} \cdot \underline{q} + \frac{q^2}{2}) - i\epsilon] |\Delta(\underline{q}, u + \frac{q^2}{2})|^2} \quad (\text{VI-44})$$

where

$$\begin{aligned} \phi(\underline{q}, u) \equiv & \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{du'}{u' - u - i\epsilon} \int d^3 v' S(u' - \underline{q} \cdot \underline{v}') Q(-\underline{q}, \underline{v}' - \frac{\underline{q}}{2}) \\ & - \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{du'}{u' - u + i\epsilon} \int d^3 v' S(u' - \underline{q} \cdot \underline{v}') Q(\underline{q}, \underline{v}' + \frac{\underline{q}}{2}) \end{aligned} \quad (\text{VI-45})$$

Using the well known relation

$$\frac{1}{x + i\epsilon} = P\left(\frac{1}{x}\right) - i\pi \delta(x) \quad (\text{VI-46})$$

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\*Note that  $\Delta$  is simply related to the R.P.A. (i.e. Hartree) dielectric constant  $\epsilon_0(\underline{q}, \omega)$  defined in III-37:

$$\Delta(\underline{q}, \underline{\Omega}) = \epsilon_0\left(\frac{m}{\hbar} \underline{q}, \frac{m}{\hbar} \left(\underline{\Omega} - \frac{q^2}{2}\right)\right)$$

we can rewrite VI-45 as

$$\begin{aligned} \phi(\underline{q}, u) &= \frac{1}{2\pi i} \oint d^3 v' [\underline{q} \cdot \underline{v}' - u]^{-1} [Q(-\underline{q}, \underline{v}' - \frac{\underline{q}}{2}) - Q(\underline{q}, \underline{v}' + \frac{\underline{q}}{2})] \\ &+ \frac{1}{2} \int d^3 v' S(u - \underline{q} \cdot \underline{v}') [Q(-\underline{q}, \underline{v}' - \frac{\underline{q}}{2}) + Q(\underline{q}, \underline{v}' + \frac{\underline{q}}{2})] \end{aligned} \quad (\text{VI-47})$$

To simplify this expression we must go back to the definition (VI-38) of  $Q$ . Noting first that from VI-33

$$\begin{aligned} S''(\underline{q}, \underline{v}_1, \underline{v}_2) &\equiv S'(\underline{q}, \underline{v}_1, \underline{v}_2) - \frac{1}{2} S'(\underline{v}_1 - \underline{v}_2 - \underline{q}, \underline{v}_1, \underline{v}_2) = \frac{g^2}{m(2\pi)^3} \left[ f(\frac{m}{\hbar} \underline{q}) - \frac{1}{2} f(\frac{m}{\hbar} |\underline{v}_1 - \underline{v}_2 - \underline{q}|) \right] \\ &\times \left\{ \tilde{F}^{(1)}(\underline{v}_1 - \underline{q}) \tilde{F}^{(1)}(\underline{v}_2 + \underline{q}) \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1) \right] \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2) \right] \right. \\ &\quad \left. - \tilde{F}^{(1)}(\underline{v}_1) \tilde{F}^{(1)}(\underline{v}_2) \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_1 - \underline{q}) \right] \left[ 1 - \frac{N\hbar^3}{2m^3} \tilde{F}^{(1)}(\underline{v}_2 + \underline{q}) \right] \right\} \end{aligned} \quad (\text{VI-48})$$

from which we deduce the symmetry property

$$S''(\underline{q}, \underline{v}_1 + \frac{\underline{q}}{2}, \underline{v}_2) = -S''(-\underline{q}, \underline{v}_1 - \frac{\underline{q}}{2}, \underline{v}_2 + \underline{q}) \quad (\text{VI-49})$$

Then

$$\begin{aligned} Q(\underline{q}, \underline{v}_1 + \frac{\underline{q}}{2}) &\equiv \frac{\int d^3 v_2 S(\underline{q}, \underline{v}_1 + \frac{\underline{q}}{2}, \underline{v}_2)}{(\underline{v}_2 - \underline{v}_1 + \frac{\underline{q}}{2}) \cdot \underline{q} - i\epsilon} = - \frac{\int d^3 v_2 S(-\underline{q}, \underline{v}_1 - \frac{\underline{q}}{2}, \underline{v}_2 + \underline{q})}{(\underline{v}_2 - \underline{v}_1 + \frac{\underline{q}}{2}) \cdot \underline{q} - i\epsilon} \\ &= \frac{\int d^3 v_2' S(-\underline{q}, \underline{v}_1 - \frac{\underline{q}}{2}, \underline{v}_2')}{-(\underline{v}_2' - \underline{v}_1 - \frac{\underline{q}}{2}) \cdot \underline{q} + i\epsilon} = Q^*(-\underline{q}, \underline{v}_1 - \frac{\underline{q}}{2}) \end{aligned} \quad (\text{VI-50})$$



where \* denotes complex conjugation. Thus,

$$\begin{aligned} \phi(\underline{q}, u) &= \frac{1}{\pi} \int d^3 v' \frac{1}{u - \underline{q} \cdot \underline{v}'} \operatorname{Im} Q(\underline{q}, \underline{v}' + \underline{q}/2) \\ &+ \int d^3 v' \delta(u - \underline{q} \cdot \underline{v}') \operatorname{Re} Q(\underline{q}, \underline{v}' + \underline{q}/2) \end{aligned} \quad (\text{VI-51})$$

which, by virtue of VI-46 may be simply written as

$$\phi(\underline{q}, u) = \frac{1}{\pi} \operatorname{Im} \left[ \int d^3 v' \frac{Q(\underline{q}, \underline{v}' + \underline{q}/2)}{u - \underline{q} \cdot \underline{v}' - i\epsilon} \right] \quad (\text{VI-52})$$

Finally, inserting this expression in VI-44 and making a variable change gives the desired result

$$\begin{aligned} P(\underline{q}, \underline{v}_1) &= \frac{Q(\underline{q}, \underline{v}_1)}{\Delta(\underline{q}, \underline{v}_1 \cdot \underline{q})} + D(\underline{q}, \underline{v}_1) \int_{-\infty}^{\infty} du \frac{1}{[u - \underline{v}_1 \cdot \underline{q} - i\epsilon] |\Delta(\underline{q}, u)|^2} \\ &\times \frac{1}{\pi} \operatorname{Im} \left\{ \int d^3 v' \frac{Q(\underline{q}, \underline{v}')}{u - \underline{q} \cdot \underline{v}' - i\epsilon} \right\} \end{aligned} \quad (\text{VI-53})$$

The full  $\mathcal{J}(\underline{q}, \underline{v}_1, \underline{v}_2)$  can now be recovered from VI-53 and VI-31. VI-29 and a Fourier inversion yield the original correlation functions G and H. Since, as we shall presently find, we only need  $P(\underline{q}, \underline{v}_1)$  for the applications in Sections C and D, VI-53 will suffice. Indeed, its real part leads to the correlation energy, its imaginary part to the collision integral.

### C. The Collision Integral

The collision integral is given in VI-9. Written in terms of  $P(\underline{q}, \underline{v}_i)$  it becomes simply

$$\left. \frac{\partial \tilde{F}^{(1)}(v_i)}{\partial t} \right|_{\text{coll.}} = \frac{i N g^2 m^3}{\hbar^4} \int d^3 q f\left(\frac{m}{\hbar} q\right) \left[ P(\underline{q}, \underline{v}_i + \underline{q}) - P(\underline{q}, \underline{v}_i) \right] \quad (\text{VI-54})$$

In our subsequent work, it will be convenient to deal with dimensionless quantities. We therefore measure all velocities (and  $q$ ) in terms of the Fermi velocity III-41. Furthermore, define

$$\tilde{F}^{(1)} \equiv \frac{2m^3}{N \hbar^3} \tilde{f}^{(1)} \quad (\text{VI-55})$$

$$P(\underline{q}, \underline{v}_i) \equiv \left( \frac{e^2 m^3}{2\pi^4 \hbar^4 N^2 v_f} \right) p(\underline{q}, \underline{v}_i) \quad (\text{VI-56})$$

and

$$\gamma \equiv \frac{t}{\hbar} R_{yd.} \equiv \frac{t m e^4}{2 \hbar^3} \quad (\text{VI-57})$$

Then introducing the specific (Coulomb) interaction via VI-32, we obtain

$$\left. \frac{\partial \tilde{f}^{(1)}(v_i)}{\partial \gamma} \right|_{\text{coll.}} = \frac{i}{\pi^4} \int \frac{d^3 q}{q^2} \left[ p(\underline{q}, \underline{v}_i + \underline{q}) - p(\underline{q}, \underline{v}_i) \right] \quad (\text{VI-58})$$

where, from VI-53 and related definitions,

$$\begin{aligned} p(\underline{q}, \underline{v}_i) = & \frac{\int d^3 v' \frac{a(\underline{q}, \underline{v}_i, v')}{(\underline{v}' - \underline{v}_i + \underline{q}) \cdot \underline{q} - i\epsilon}}{\Delta(\underline{q}, \underline{v}_i, \underline{q})} + D(\underline{q}, \underline{v}_i) \int_{-\infty}^{\infty} \frac{du}{[u - \underline{v}_i \cdot \underline{q} - i\epsilon] |\Delta(\underline{q}, \omega)|^2} \\ & \times \frac{1}{\pi} \text{Im} \left\{ \int \frac{d^3 v'}{u - \underline{q} \cdot \underline{v}' - i\epsilon} \int \frac{d^3 v'' a(\underline{q}, v', v'')}{(\underline{v}'' - \underline{v}' + \underline{q}) \cdot \underline{q} - i\epsilon} \right\} \end{aligned} \quad (\text{VI-59})$$

all quantities now being dimensionless. In the above,

$$A(q, \underline{v}, \underline{v}') \equiv \left( \frac{1}{q^2} - \frac{1}{2(\underline{v} - \underline{v}' - \underline{q})^2} \right) \left\{ \tilde{f}^{(1)}(\underline{v} - \underline{q}) \tilde{f}^{(1)}(\underline{v}' + \underline{q}) [1 - \tilde{f}^{(1)}(\underline{v})] [1 - \tilde{f}^{(1)}(\underline{v}')] \right. \\ \left. - \tilde{f}^{(1)}(\underline{v}) \tilde{f}^{(1)}(\underline{v}') [1 - \tilde{f}^{(1)}(\underline{v} - \underline{q})] [1 - \tilde{f}^{(1)}(\underline{v}' + \underline{q})] \right\}$$

$$D(q, \underline{v}) \equiv \frac{\alpha r_s}{\pi^2 q^2} \left[ \tilde{f}^{(1)}(\underline{v} - \underline{q}) - \tilde{f}^{(1)}(\underline{v}) \right] \quad \alpha \equiv \left( \frac{4}{9\pi} \right)^{1/3} \quad (\text{VI-60})$$

$$= \frac{\alpha r_s}{\pi^2 q^2} \left\{ \tilde{f}^{(1)}(\underline{v} - \underline{q}) [1 - \tilde{f}^{(1)}(\underline{v})] - \tilde{f}^{(1)}(\underline{v}) [1 - \tilde{f}^{(1)}(\underline{v} - \underline{q})] \right\} \quad (\text{VI-61})$$

and

$$\Delta(q, \Omega) \equiv 1 + \frac{\int d^3 v' D(q, \underline{v}')}{\Omega + \underline{q} \cdot (\underline{v}' - \underline{q}) + i\epsilon} \quad (\text{VI-62})$$

where  $r_s$  is defined in IV-115.

After relatively straightforward though somewhat tedious algebra, one can establish from VI-59 - VI-62 the symmetry property

$$\rho(q, \underline{v} + \underline{q}) = \rho^*(-q, \underline{v}) \quad (\text{VI-63})$$

so that VI-58 becomes simply

$$\left. \frac{\partial \tilde{f}^{(1)}(v)}{\partial v} \right|_{\text{coll.}} = \frac{2}{\pi^4} \text{Im} \int \frac{d^3 q}{q^2} \rho(q, \underline{v}) = \frac{2}{\pi^4} \int \frac{d^3 q}{q^2} \rho(-q, \underline{v}) \quad (\text{VI-64})$$

It is slightly more convenient to deal with  $\rho(-q, \underline{v})$  than  $\rho(q, \underline{v})$ , so the latter form of VI-64 will be used. Employing VI-46 and performing



the  $u$  integration in VI-59 leads after some manipulation to

$$\begin{aligned}
 \text{Im } \rho(-\underline{q}, \underline{v}) &= \frac{\pi}{|\Delta(-\underline{q}, -\underline{v}, \underline{q})|^2} \left\{ \int d^3 v' \mathcal{S}((\underline{v}' + \underline{v} + \underline{q}) \cdot \underline{q}) a(-\underline{q}, \underline{v}, -\underline{v}') \right. \\
 &+ \left[ \int d^3 v' \frac{a(-\underline{q}, \underline{v}, -\underline{v}')}{(\underline{v} + \underline{v}' + \underline{q}) \cdot \underline{q}} \right] \left[ \int d^3 v'' \mathcal{S}((\underline{v} + \underline{v}'' + \underline{q}) \cdot \underline{q}) \mathcal{D}(-\underline{q}, \underline{v}'') \right] \\
 &- \left[ \int d^3 v' \mathcal{S}((\underline{v}' + \underline{v} + \underline{q}) \cdot \underline{q}) a(-\underline{q}, \underline{v}, -\underline{v}') \right] \left[ \int d^3 v'' \frac{\mathcal{D}(-\underline{q}, \underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{q}) \cdot \underline{q}} \right] \quad (\text{VI-65}) \\
 &+ \mathcal{D}(-\underline{q}, \underline{v}) \left[ \iint d^3 v' d^3 v'' \mathcal{S}((\underline{v} - \underline{v}') \cdot \underline{q}) \frac{a(-\underline{q}, \underline{v}', -\underline{v}'')}{(\underline{v}' + \underline{v}'' + \underline{q}) \cdot \underline{q}} \right] \\
 &+ \mathcal{D}(-\underline{q}, \underline{v}) \left[ \iint d^3 v' d^3 v'' \frac{1}{(\underline{v}' - \underline{v}) \cdot \underline{q}} \mathcal{S}((\underline{v}' + \underline{v}'' + \underline{q}) \cdot \underline{q}) a(-\underline{q}, \underline{v}', -\underline{v}'') \right] \Big\}
 \end{aligned}$$

Turning first to the last term of VI-65, we note from the definition VI-60 that it may be written

$$\begin{aligned}
 \mathcal{D}(-\underline{q}, \underline{v}) &\left\{ \iint d^3 v' d^3 v'' \frac{\mathcal{S}((\underline{v}' + \underline{v}'' + \underline{q}) \cdot \underline{q})}{(\underline{v}' - \underline{v}) \cdot \underline{q}} \left[ \frac{1}{q^2} - \frac{1}{2(\underline{v}' + \underline{v}'' + \underline{q})^2} \right] \tilde{f}^{(1)}(\underline{v}' + \underline{q}) \tilde{f}^{(1)}(\underline{v}'' + \underline{q}) \right. \\
 &\times [1 - \tilde{f}^{(1)}(\underline{v}')] [1 - \tilde{f}^{(1)}(\underline{v}'')] - \iint d^3 v' d^3 v'' \frac{\mathcal{S}((\underline{v}' + \underline{v}'' + \underline{q}) \cdot \underline{q})}{(\underline{v}' - \underline{v}) \cdot \underline{q}} \left[ \frac{1}{q^2} - \frac{1}{2(\underline{v}' + \underline{v}'' + \underline{q})^2} \right] \tilde{f}^{(1)}(\underline{v}') \tilde{f}^{(1)}(\underline{v}'') \\
 &\times [1 - \tilde{f}^{(1)}(\underline{v}' + \underline{q})] [1 - \tilde{f}^{(1)}(\underline{v}'' + \underline{q})] \Big\} \quad (\text{VI-66})
 \end{aligned}$$

Making the variable changes  $\underline{v}' = -\underline{v}''' - \underline{q}$  and  $\underline{v}'' = -\underline{v}'''' - \underline{q}$  converts the second term of VI-66 into

$$\begin{aligned}
 &- \iint d^3 v''' d^3 v'''' \frac{\mathcal{S}((\underline{v}''' + \underline{v}'''' + \underline{q}) \cdot \underline{q})}{(-\underline{v}''' - \underline{v}'''' - \underline{q}) \cdot \underline{q}} \left[ \frac{1}{q^2} - \frac{1}{2(\underline{v}''' + \underline{v}'''' + \underline{q})^2} \right] \\
 &\times \tilde{f}^{(1)}(\underline{v}''' + \underline{q}) \tilde{f}^{(1)}(\underline{v}'''' + \underline{q}) [1 - \tilde{f}^{(1)}(\underline{v}''')] [1 - \tilde{f}^{(1)}(\underline{v}''')] \quad (\text{VI-67})
 \end{aligned}$$

which by virtue of the delta function can be rewritten as

$$- \iint d^3 v''' d^3 v'''' \frac{\delta((v''' + v'''' + \xi) \cdot \xi)}{(v''' - v'') \cdot \xi} \left[ \frac{1}{\xi^2} - \frac{1}{2(v''' + v'''' + \xi)^2} \right] \tilde{f}^{(1)}(v''' + \xi) \tilde{f}^{(1)}(v'''' + \xi) \\ \times [1 - \tilde{f}^{(1)}(v''')] [1 - \tilde{f}^{(1)}(v'')] \quad (\text{VI-68})$$

Finally, changing dummy variables  $v''' \rightarrow v'$ ,  $v'''' \rightarrow v''$ , reveals that VI-68 exactly cancels the first term of VI-66 so that the last term of VI-65 vanishes identically.

In treating the remainder of VI-65, it is both instructive and convenient to separate the exchange and non-exchange contributions. Specifically, let

$$\text{dm } p(-\xi, v) \equiv \text{dm } p_0(-\xi, v) + \text{dm } p_1(-\xi, v) \quad (\text{VI-69})$$

and introduce the shorthand

$$f^+(v) \equiv \tilde{f}^{(1)}(v + \xi) [1 - \tilde{f}^{(1)}(v)] \\ f^-(v) \equiv \tilde{f}^{(1)}(v) [1 - \tilde{f}^{(1)}(v + \xi)] \quad (\text{VI-70})$$

Then making use of VI-60 and VI-61, we obtain for the non-exchange component

$$\text{dm } p_0(-\xi, v) = \frac{\pi}{|\Delta(-\xi, -v, \xi)|^2} \cdot \frac{1}{\xi^2} \int d^3 v' \delta((v' + v + \xi) \cdot \xi) [f^+(v) f^+(v') - f^-(v) f^-(v')] \\ + \frac{\pi}{|\Delta(-\xi, -v, \xi)|^2} \frac{\alpha r_s}{\pi^2 \xi^4} \left\{ \left[ \int d^3 v' \frac{f^+(v) f^+(v') - f^-(v) f^-(v')}{(v + v' + \xi) \cdot \xi} \right] \left[ \int d^3 v'' \delta((v + v'' + \xi) \cdot \xi) (f^+(v'') - f^-(v'')) \right] \right. \\ \left. - \left[ \int d^3 v' \delta((v' + v + \xi) \cdot \xi) (f^+(v) f^+(v') - f^-(v) f^-(v')) \right] \left[ \int d^3 v'' \frac{f^+(v'') - f^-(v'')}{(v + v'' + \xi) \cdot \xi} \right] \right. \\ \left. + (f^+(v) - f^-(v)) \int \int d^3 v' d^3 v'' \delta((v - v') \cdot \xi) \frac{(f^+(v') f^+(v'') - f^-(v') f^-(v''))}{(v' + v'' + \xi) \cdot \xi} \right\}$$

Similarly, for the part originating from exchange collisions we obtain

$$\begin{aligned}
 dm \, p_1(-\underline{q}, \underline{v}) = & \frac{\pi}{|\Delta(-\underline{q}, -\underline{v}, \underline{g})|^2} \left(-\frac{1}{2}\right) \int d^3 v' \frac{\delta((\underline{v}' + \underline{v} + \underline{g}) \cdot \underline{g})}{(\underline{v} + \underline{v}' + \underline{g})^2} [f^+(\underline{v}) f^+(\underline{v}') - f^-(\underline{v}) f^-(\underline{v}')] \\
 & + \frac{\pi}{|\Delta(-\underline{q}, -\underline{v}, \underline{g})|^2} \frac{\alpha r_s}{\pi^2 g^2} \left(-\frac{1}{2}\right) \left\{ \left[ \int d^3 v' \frac{f^+(\underline{v}') - f^-(\underline{v}')}{(\underline{v} + \underline{v}' + \underline{g})^2 (\underline{v} + \underline{v}' + \underline{g}) \cdot \underline{g}} \right] \left[ \int d^3 v'' \frac{\delta((\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g})}{(\underline{v} + \underline{v}'' + \underline{g})^2} (f^+(\underline{v}') - f^-(\underline{v}')) \right] \right. \\
 & - \left[ \int d^3 v' \frac{\delta((\underline{v}' + \underline{v} + \underline{g}) \cdot \underline{g})}{(\underline{v} + \underline{v}' + \underline{g})^2} (f^+(\underline{v}) f^+(\underline{v}') - f^-(\underline{v}) f^-(\underline{v}')) \right] \left[ \int d^3 v'' \frac{f^+(\underline{v}'') - f^-(\underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right] \\
 & \left. + [f^+(\underline{v}) - f^-(\underline{v})] \int \int d^3 v' d^3 v'' \frac{\delta((\underline{v} - \underline{v}') \cdot \underline{g})}{(\underline{v}' + \underline{v}'' + \underline{g})^2} \frac{(f^+(\underline{v}') f^+(\underline{v}'') - f^-(\underline{v}') f^-(\underline{v}''))}{(\underline{v}' + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right\}
 \end{aligned}$$

(VI-72)

We consider first VI-71, and observe that by virtue of the delta function the last term can be rewritten as\*

$$\begin{aligned}
 [f^+(\underline{v}) - f^-(\underline{v})] & \left[ \left( \int d^3 v' \frac{\delta((\underline{v} - \underline{v}') \cdot \underline{g})}{(\underline{v}' + \underline{v}'' + \underline{g})^2} f^+(\underline{v}') \right) \left( \int d^3 v'' \frac{f^+(\underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right) \right. \\
 & \left. - \left( \int d^3 v' \frac{\delta((\underline{v} - \underline{v}') \cdot \underline{g})}{(\underline{v}' + \underline{v}'' + \underline{g})^2} f^-(\underline{v}') \right) \left( \int d^3 v'' \frac{f^-(\underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right) \right]
 \end{aligned}$$

(VI-73)

Then, making the variable change  $\underline{v}' \rightarrow -\underline{v}''' - \underline{g}$  reduces this to

$$\begin{aligned}
 [f^+(\underline{v}) - f^-(\underline{v})] & \left[ \left( \int d^3 v'' \frac{\delta((\underline{v} + \underline{v}''' + \underline{g}) \cdot \underline{g})}{(\underline{v} + \underline{v}'' + \underline{g})^2} f^-(\underline{v}''') \right) \left( \int d^3 v'' \frac{f^+(\underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right) \right. \\
 & \left. - \left( \int d^3 v'' \frac{\delta((\underline{v} + \underline{v}''' + \underline{g}) \cdot \underline{g})}{(\underline{v} + \underline{v}'' + \underline{g})^2} f^+(\underline{v}''') \right) \left( \int d^3 v'' \frac{f^-(\underline{v}'')}{(\underline{v} + \underline{v}'' + \underline{g}) \cdot \underline{g}} \right) \right]
 \end{aligned}$$

(VI-74)

\*This separation of the double integral into a product of single integrals will not be possible in the corresponding term of VI-72, a circumstance which underlies our separate treatment of exchange.



The terms occurring within the curly bracket of VI-71 can now be combined and one easily finds that they all mutually cancel. Thus

$$\text{Im } \rho_0(-\underline{q}, \underline{v}) = \frac{\pi}{|\Delta(-\underline{q}, -\underline{v}, \underline{q})|^2} \frac{1}{q^2} \int d^3 v' \delta((\underline{v} + \underline{v}' + \underline{q}) \cdot \underline{q}) [f^+(\underline{v}) f^+(\underline{v}') - f^-(\underline{v}) f^-(\underline{v}')] \quad (\text{VI-75})$$

Before evaluating the exchange contribution, VI-72, it is worthwhile to collect the results obtained thus far. Inserting VI-75 into VI-64 and changing from  $\underline{v}' \rightarrow -\underline{v}'$  yields

$$\begin{aligned} \left. \frac{\partial \tilde{f}^{(1)}(\underline{v})}{\partial \tau} \right|_{\text{coll.}} &= -\frac{2}{\pi^3} \int d^3 \underline{q} \int d^3 v' \left| \frac{1}{q^2 \Delta(-\underline{q}, -\underline{v}, \underline{q})} \right|^2 \delta((\underline{v} - \underline{v}' + \underline{q}) \cdot \underline{q}) \\ &\times \left\{ \tilde{f}^{(1)}(\underline{v}) \tilde{f}^{(1)}(\underline{v}') [1 - \tilde{f}^{(1)}(\underline{v} + \underline{q})] [1 - \tilde{f}^{(1)}(\underline{v}' - \underline{q})] - \tilde{f}^{(1)}(\underline{v} + \underline{q}) \tilde{f}^{(1)}(\underline{v}' - \underline{q}) [1 - \tilde{f}^{(1)}(\underline{v})] [1 - \tilde{f}^{(1)}(\underline{v}')] \right\} \\ &+ \text{exchange term} \end{aligned} \quad (\text{VI-76})$$

The physical significance of this result is clarified if we first recall that

$$\Delta(-\underline{q}, -\underline{v}, \underline{q}) = \epsilon_0 \left( -\frac{m}{\hbar} \underline{q}, -\frac{m}{\hbar} (\underline{v} \cdot \underline{q} + \frac{q^2}{2}) \right) = \epsilon_0^* \left( \frac{m}{\hbar} \underline{q}, \frac{m}{\hbar} (\underline{v} \cdot \underline{q} + \frac{q^2}{2}) \right) \quad (\text{VI-77})$$

where  $\epsilon_0(k, \omega)$  is the wave number and frequency dependent dielectric constant of the electron gas as computed in the Hartree (or "Random Phase") approximation (see III-37):

$$\epsilon_0(k, \omega) = \left| -\frac{\alpha r_s}{\pi^2 k^2} \frac{m^3}{\hbar^3} \int d^3 v' \frac{\tilde{f}^{(1)}(\underline{v}') - \tilde{f}^{(1)}(\underline{v}' + \frac{\hbar}{m} \underline{k})}{\omega - \hbar \cdot \underline{v}' - \frac{\hbar^2 k^2}{2m} + i\epsilon} \right| \quad (\text{VI-78})$$

Then if we switch from velocity space to wave vector space

$$\hbar \underline{p} \equiv m \underline{v} \quad \tilde{f}^{(1)}(\underline{p}) d^3 p \equiv \tilde{f}^{(1)}(\underline{v}) d^3 v \quad (\text{VI-79})$$

and introduce the kinetic energy

$$E(p) \equiv \frac{\hbar^2 p^2}{2m} \quad (\text{VI-80})$$

we find that VI-76 becomes (in dimensional time)

$$\begin{aligned} \left. \frac{\partial \tilde{f}^{(n)}(p)}{\partial t} \right|_{\text{coll.}} = & -\frac{2\pi}{\hbar} \cdot (2) \cdot \int \frac{d^3 p'}{(2\pi)^3} \int \frac{d^3 q}{(2\pi)^3} \left| \frac{4\pi e^2}{q^2 \epsilon_0 \left( \frac{m}{\hbar} q, \frac{1}{\hbar} (E(p+q) - E(p)) \right)} \right|^2 \\ & \times \delta [E(p+q) + E(p'-q) - E(p) - E(p')] \times \left\{ \tilde{f}^{(n)}(p) \tilde{f}^{(n)}(p') [1 - \tilde{f}^{(n)}(p+q)] [1 - \tilde{f}^{(n)}(p'-q)] \right. \\ & \left. - \tilde{f}^{(n)}(p+q) \tilde{f}^{(n)}(p'-q) [1 - \tilde{f}^{(n)}(p)] [1 - \tilde{f}^{(n)}(p')] \right\} \\ & + \text{exchange term} \end{aligned} \quad (\text{VI-81})$$

Neglecting for the moment the extra factor of two, this is recognized to be just the "golden rule" for the transition probability per unit time for the scattering of electrons from states  $(p, p')$  to  $(p+q, p'-q)$  (less, of course, the inverse process) where the matrix element is given by

$$\langle p, p' | M | p+q, p'-q \rangle = \frac{4\pi e^2}{q^2 \epsilon_0 \left( \frac{m}{\hbar} q, \frac{1}{\hbar} (E(p+q) - E(p)) \right)} \quad (\text{VI-82})$$

i.e., the matrix element for Coulomb scattering divided by the dynamical dielectric constant of the medium.

Thus, on the basis of the plausible conjecture that correlation effects simply screen the basic scattering process in the manner given by VI-82, the collision integral in the absence of exchange interactions could have been written down at once, as indeed was done in a recent paper by Wyld and Pines (19). The first derivation of VI-76 was apparently given by Silin (86) using methods similar to ours. It was also obtained by Guernsey (18) despite

a significant error\* in his derivation. The exchange contribution which we are about to derive, on the other hand, has not (to our knowledge) been previously calculated nor, as we shall see, do the dielectric properties of the medium enter in so transparent a fashion.

Returning to VI-72, the first and third terms can be immediately combined to yield

$$-\frac{1}{2} \frac{\pi}{|\Delta(-\xi, -\underline{v} \cdot \underline{\xi})|^2} \int d^3 v' \frac{\delta((\underline{v}' + \underline{v} + \underline{\xi}) \cdot \underline{\xi})}{(\underline{v}' + \underline{v} + \underline{\xi})^2} [f^+(\underline{v}) f^+(\underline{v}') - f^-(\underline{v}) f^-(\underline{v}')] \times \left\{ 1 - \frac{\alpha r_s}{\pi^2 q^2} \int d^3 v'' \frac{f^+(\underline{v}'') - f^-(\underline{v}'')}{(\underline{v}' + \underline{v}'' + \underline{\xi}) \cdot \underline{\xi}} \right\} \quad (\text{VI-83})$$

But from the definition VI-62, the term in curly brackets is seen to be just  $\text{Re} [\Delta(-\xi, -\underline{v} \cdot \underline{\xi})]$ . Hence VI-83 becomes

$$-\frac{\pi}{2} \text{Re} \left( \frac{1}{\Delta(-\xi, -\underline{v} \cdot \underline{\xi})} \right) \int d^3 v' \frac{\delta((\underline{v}' + \underline{v} + \underline{\xi}) \cdot \underline{\xi})}{(\underline{v}' + \underline{v} + \underline{\xi})^2} [f^+(\underline{v}) f^+(\underline{v}') - f^-(\underline{v}) f^-(\underline{v}')] \quad (\text{VI-84})$$

Making the variable changes  $\underline{v}' \leftrightarrow \underline{v}''$  in the second term of VI-62 and  $\underline{v}' \rightarrow -\underline{v}' - \underline{\xi}$ ,  $\underline{v}'' \rightarrow -\underline{v}'' - \underline{\xi}$  in the last term yields the remaining contribution

$$-\frac{\pi}{2} \frac{\alpha r_s}{\pi^2 q^2} \frac{1}{|\Delta(-\xi, -\underline{v} \cdot \underline{\xi})|^2} \int d^3 v' \delta((\underline{v}' + \underline{v} + \underline{\xi}) \cdot \underline{\xi}) \left\{ [f^+(\underline{v}') - f^-(\underline{v}')] \int d^3 v'' \frac{f^+(\underline{v}) f^+(\underline{v}'') - f^-(\underline{v}) f^-(\underline{v}'')}{(\underline{v}' + \underline{v}'' + \underline{\xi})^2 (\underline{v}' + \underline{v}'' + \underline{\xi}) \cdot \underline{\xi}} \right. \\ \left. + [f^+(\underline{v}) - f^-(\underline{v})] \int d^3 v'' \frac{f^+(\underline{v}') f^+(\underline{v}'') - f^-(\underline{v}') f^-(\underline{v}'')}{(\underline{v}' + \underline{v}'' + \underline{\xi})^2 (\underline{v}'' + \underline{v}' + \underline{\xi}) \cdot \underline{\xi}} \right\} \quad (\text{VI-85})$$

\*Equation (46) of his paper should read

$$\bar{q}(u, k) = \bar{q}^*(-u, -k)$$

and his expression (47) for the correlation function is consequently both incorrect and incapable of yielding his (correct) collision integral.



Making the variable changes  $\underline{v}' \rightarrow -\underline{v}'$ ,  $\underline{v}'' \rightarrow -\underline{v}''$  in VI-84 and VI-85 and combining them with VI-76 leads to final desired result for the total collision integral:

$$\begin{aligned} \left. \frac{\partial \tilde{f}^{(n)}(v)}{\partial \tau} \right|_{\text{coll.}} = & -\frac{2}{\pi^3} \int d^3 \underline{q} \int d^3 \underline{v}' \delta(\underline{q} \cdot (\underline{v} - \underline{v}' + \underline{q})) \left\{ \left[ \frac{1}{\epsilon^4 |\Delta(-\underline{q}, -\underline{v}, \underline{q})|^2} \right. \right. \\ & \left. \left. - \frac{1}{2\epsilon^2 (\underline{v} - \underline{v}' + \underline{q})^2} \operatorname{Re} \left( \frac{1}{\Delta(-\underline{q}, -\underline{v}, \underline{q})} \right) \right] \times T(\underline{v}, \underline{v}', \underline{q}) \right\} + \left\{ \left[ \frac{\alpha r_s}{2\pi^2 \epsilon^4 |\Delta(-\underline{q}, -\underline{v}, \underline{q})|^2} \right. \right. \\ & \times \left[ (\tilde{f}^{(n)}(v') - \tilde{f}^{(n)}(\underline{v}' - \underline{q})) \int d^3 \underline{v}'' \frac{T(\underline{v}, \underline{v}'', \underline{q})}{(\underline{v} - \underline{v}'' + \underline{q})^2 (\underline{v} - \underline{v}'' + \underline{q}) \cdot \underline{q}} \right. \\ & \left. \left. + (\tilde{f}^{(n)}(v) - \tilde{f}^{(n)}(\underline{v} + \underline{q})) \int d^3 \underline{v}'' \frac{T(\underline{v}'', \underline{v}', \underline{q})}{(\underline{v}'' - \underline{v}' + \underline{q})^2 (\underline{v}'' - \underline{v}' + \underline{q}) \cdot \underline{q}} \right] \right\} \end{aligned} \quad (\text{VI-86})$$

where

$$\begin{aligned} T(\underline{v}, \underline{v}', \underline{q}) \equiv & \tilde{f}^{(n)}(v) \tilde{f}^{(n)}(v') [1 - \tilde{f}^{(n)}(\underline{v} + \underline{q})] [1 - \tilde{f}^{(n)}(\underline{v}' - \underline{q})] \\ & - \tilde{f}^{(n)}(\underline{v} + \underline{q}) \tilde{f}^{(n)}(\underline{v}' - \underline{q}) [1 - \tilde{f}^{(n)}(v)] [1 - \tilde{f}^{(n)}(v')] \end{aligned} \quad (\text{VI-87})$$

The physical significance of the new terms are easily understood. Those in the second set of curly brackets represent ordinary Coulomb scattering ("dressed", however, by the dielectric behaviour of the system in the fashion of VI-82) with a virtual exchange scattering (via the "bare" Coulomb interaction) between one of the two incoming (or outgoing) particles and a third particle of the system.

The additional term in the first set of curly brackets can be clarified if we momentarily ignore the dielectric constant and consider the spin

averaged matrix element (squared) for the Coulomb scattering of two free electrons, taking account, however, of exchange (i.e. "Mott" scattering). For initial velocities  $\underline{v}, \underline{v}'$  and momentum transfer  $\underline{q}$ , we have in Born Approximation:

$$\begin{aligned} |\langle \underline{v}, \underline{v}' | M | \underline{v} + \underline{q}, \underline{v}' - \underline{q} \rangle|^2 &= (4\pi e^2)^2 \left\{ \frac{3}{4} \left( \frac{1}{q^2} - \frac{1}{(\underline{v} - \underline{v}' + \underline{q})^2} \right)^2 \right. \\ &\quad \left. + \frac{1}{4} \left( \frac{1}{q^2} + \frac{1}{(\underline{v} - \underline{v}' + \underline{q})^2} \right)^2 \right\} = (4\pi e^2)^2 \left\{ \frac{1}{q^4} + \frac{1}{(\underline{v} - \underline{v}' + \underline{q})^4} - \frac{1}{q^2(\underline{v} - \underline{v}' + \underline{q})^2} \right\} \\ &\quad (m \equiv 1) \end{aligned} \quad (\text{VI-88})$$

By symmetry, the first two terms of VI-88 give equal contributions to the collision integral so we have, in effect,

$$|\langle \underline{v}, \underline{v}' | M | \underline{v} + \underline{q}, \underline{v}' - \underline{q} \rangle|^2 = (4\pi e^2)^2 \cdot 2 \cdot \left\{ \frac{1}{q^4} - \overbrace{\frac{1}{2q^2(\underline{v} - \underline{v}' + \underline{q})^2}}^{\text{"Mott" term}} \right\} \quad (\text{VI-89})$$

Recalling the extra factor of 2 in VI-81, we see that in the limit  $\Delta \rightarrow 1$  VI-89 yields exactly the first group of terms in VI-86. This, of course, must be so since we could have written down (using the "golden rule") the formal perturbation series for  $\frac{\partial \tilde{f}^{(1)}}{\partial t}$ , the lowest order terms of which are just VI-89. What could not have been anticipated, however, is the peculiar fashion in which the dielectric constant enters in the "Mott" term of VI-86.

Setting VI-86 equal to zero yields an equation for the equilibrium  $\tilde{f}^{(0)}$ . It is easily shown that

$$\delta(\underline{q} \cdot (\underline{v} - \underline{v}' + \underline{q})) T(\underline{v}, \underline{v}', \underline{q}) = 0 \quad (\text{VI-90})$$

if  $\tilde{f}^{(n)}$  has the Fermi form

$$\tilde{f}^{(n)}(v) = [\exp(Av^2 - B) + 1]^{-1} \quad (\text{VI-91})$$

so that the first curly bracketed term of VI-86 does indeed identically vanish for the Fermi distribution, thereby redeeming an earlier promise that VI-91 can be obtained without recourse to an H-theorem or ensemble theory. The second curly bracketed term, however, does not apparently vanish for VI-91\* and we are thus led to the expectation that VI-86 will generate an  $r_s$  dependent modification of the Fermi distribution. That exchange effects do indeed "smear out" the Fermi surface, even at zero temperature, is known from field theoretic studies (87) of the problem.

In the high density limit:

$$r_s \rightarrow 0 \quad \Delta \rightarrow 1 \quad (\text{VI-92})$$

the collision integral which becomes simply (changing  $\tilde{v}' \rightarrow -\tilde{v}'$  for convenience)

$$\begin{aligned} \frac{\partial \tilde{f}^{(n)}(v)}{\partial \tau} \Big|_{\text{coll.}} \Big|_{r_s \rightarrow 0} &= -\frac{2}{\pi^3} \int d^3q \int d^3v' \delta(\underline{q} \cdot (\underline{v} + \underline{v}' + \underline{q})) \left[ \frac{1}{q^4} - \frac{1}{2q^2(\underline{v} + \underline{v}' + \underline{q})^2} \right] \\ &\times \left\{ \tilde{f}^{(n)}(v) \tilde{f}^{(n)}(v') [1 - \tilde{f}^{(n)}(\underline{v} + \underline{q})] [1 - \tilde{f}^{(n)}(\underline{v}' + \underline{q})] - \tilde{f}^{(n)}(\underline{v} + \underline{q}) \tilde{f}^{(n)}(\underline{v}' + \underline{q}) [1 - \tilde{f}^{(n)}(v)] [1 - \tilde{f}^{(n)}(v')] \right\} \end{aligned} \quad (\text{VI-93})$$

does, as has been observed, vanish for the Fermi distribution. Due, however, to the added "Mott" term which has been shown to arise from the interference between direct and exchange scattering, the interesting possibility arises that VI-91 may no longer\*\*be the only  $\tilde{f}^{(n)}$  which makes the collision integral

\*This is not in conflict with the H-theorem since it represents in effect a three-body collision process.

\*\*In the absence of the "Mott" term, the uniqueness of VI-91 follows directly from the non-negativity of .



vanish. If indeed this is the case, the ground state of the system would be that solution of VI-93 which has the lowest total energy. Since the kinetic and exchange energies have a different dependence on both  $\tilde{f}^{(1)}$  and  $\zeta_s$ , the possibility would then arise that the ground state of the system might have a structure different from VI-91 for some values of  $\zeta_s$ , even in the absence of the three-body terms in VI-86. Inclusion of the dielectric constants in VI-93 would even further complicate the equation and make the uniqueness of the Fermi distribution correspondingly more suspect. This conjecture seems particularly worthy of further study since, for a given  $q$  the "Mott" term of VI-93 is seen to represent an effective attractive interaction which is strongest for pairs of particles the sum of whose velocities is  $-\frac{q}{\hbar}$ , an interaction similar in some respects to that between "Cooper pairs", postulated on entirely different physical grounds in the BCS (88) theory of superconductivity.

#### D. The Correlation Energy

The interaction energy density of the system is obtained, in general, from the second term of IV-73. Using III-20, VI-3, VI-4, VI-7, VI-10, VI-18 and VI-36, one finds it can be concisely written as

$$E_{int} = \text{Re} \left\{ -\frac{q^2}{4} \int d^3v_1 d^3v_2 f\left(\frac{m}{\hbar}(v_1 - v_2)\right) (N\tilde{F}^{(1)}(v_1))(N\tilde{F}^{(1)}(v_2)) \right. \\ \left. + \frac{q^2 N^2 m^3}{2 \hbar^3} \int d^3q d^3v f\left(\frac{m}{\hbar}q\right) P(q, v) \right\} \quad (\text{VI-94})$$

where the first term is the exchange energy density and the second is the change\* in the interaction energy caused by correlations. The electron-

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\*The formally infinite energy density arising from the "self-consistent field" is cancelled by that due to the uniform charge background.

electron interactions also change the kinetic energy density due to the fact that  $\tilde{F}^{(1)}$  will be altered when all correlations are properly taken into account. For a system in an energy eigenstate, however, a powerful theorem credited to Pauli and independently discovered by (among others) Feynman (89) and Sawada (90) relates the total energy density of the system to an integral of the interaction energy over the coupling constant,  $g^2$ . Specifically\*,

$$\epsilon_{\text{TOTAL}}(g^2) = \epsilon_{\text{TOTAL}}(g^2=0) + \int_0^{g^2} \frac{\epsilon_{\text{int}}(g'^2)}{g'^2} dg'^2 \quad (\text{VI-95})$$

where the first term is the energy density in the absence of interactions, i.e., the kinetic energy density of free particles.

Now, in order to evaluate  $\epsilon_{\text{int}}$ , we must have a specific form for  $\tilde{F}^{(1)}$ . Since we have shown in the previous section that aside from higher order three-body processes the Fermi-Dirac distribution leads to the vanishing of the collision integral, this is what will be used. It must be emphasized, however, that the uniqueness of the Fermi distribution has not yet been established and, furthermore, that a more exact calculation of the energy must take account of the  $r_s$  (i.e.  $g^2$ ) dependent alterations of  $\tilde{F}^{(1)}$  caused by the three-body terms in the collision integral.

Since the Fermi distribution is independent of  $g^2$ , the ordinary exchange energy density (the first term of VI-94) is linear in  $g^2$  and hence is not changed by the integration in VI-95. Thus, if we define the correlation energy density,  $\epsilon_{\text{corr}}$ , as the difference between  $\epsilon_{\text{total}}(g^2)$  and

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\*We assume, of course, a constant volume system. Since VI-95 holds for any system in an energy eigenstate, it will be true for each member of a canonical ensemble and hence applies at non-zero temperatures where the  $\epsilon$ 's are then understood to represent ensemble averaged quantities. See, e.g., Englert and Brout (91).

that given by the Hartree-Fock approximation (see Chapter IV), we then have

$$\epsilon_{\text{corr}}(g^2) = \int_0^{g^2} \frac{\epsilon_{\text{int}}^{\text{corr}}(g'^2)}{g'^2} dg'^2 \quad (\text{VI-96})$$

where

$$\epsilon_{\text{int}}^{\text{corr}}(g^2) \equiv \text{Re} \frac{g^2 N^2 m^3}{2 \hbar^3} \int d^3 \underline{\xi} d^3 \underline{v} f\left(\frac{m}{\hbar} \underline{\xi}\right) \mathcal{P}(\underline{\xi}, \underline{v}) \quad (\text{VI-97})$$

Furthermore, since

$$\epsilon_{\text{corr}}(g^2) = \epsilon_{\text{int}}^{\text{corr}}(g^2) + \epsilon_{\text{kin}}^{\text{corr}}(g^2) \quad (\text{VI-98})$$

where  $\epsilon_{\text{kin}}^{\text{corr}}$  is the change in kinetic energy density caused by correlations, then

$$\epsilon_{\text{kin}}^{\text{corr}}(g^2) = \left[ \int_0^{g^2} \frac{d g'^2}{g'^2} \epsilon_{\text{int}}^{\text{corr}}(g'^2) \right] - \epsilon_{\text{int}}^{\text{corr}}(g^2) \quad (\text{VI-99})$$

the potential utility of which will be discussed at the end of the chapter.

Having thus dispensed with the preliminaries, we now turn to the evaluation of VI-97, using the expression VI-53 for  $\mathcal{P}$  and the Fermi distribution for  $\tilde{f}^{(1)}$ . Noting first that the vanishing of the (two body part of the) collision integral for the Fermi distribution is tantamount to (see Section c)

$$\text{Im } Q(\underline{\xi}, \underline{v}) = 0 \quad (\text{VI-100})$$

a fact which can also readily be established from the definitions VI-38, VI-46 and VI-48, we have

$$\frac{1}{\pi} \text{Im} \left\{ \int d^3 \underline{v}' \frac{Q(\underline{\xi}, \underline{v}')}{u - \underline{\xi} \cdot \underline{v}' - i\epsilon} \right\} = \int d^3 \underline{v}' \delta(u - \underline{\xi} \cdot \underline{v}') Q(\underline{\xi}, \underline{v}') \quad (\text{VI-101})$$



Performing the  $u$  integration in VI-53 yields

$$P(\underline{q}, \underline{v}) = \frac{Q(\underline{q}, \underline{v})}{\Delta(\underline{q}, \underline{v}; \underline{q})} + D(\underline{q}, \underline{v}) \int d^3 v' \frac{Q(\underline{q}, \underline{v}')}{[(\underline{v}' - \underline{v}) \cdot \underline{q} - i\epsilon] |\Delta(\underline{q}, \underline{v}; \underline{q})|^2} \quad (\text{VI-102})$$

Then, integrating VI-102 over  $\underline{v}$  and interchanging  $\underline{v}$  and  $\underline{v}'$  in the second term yields

$$\int P(\underline{q}, \underline{v}) d^3 v = \int d^3 v \frac{Q(\underline{q}, \underline{v})}{|\Delta(\underline{q}, \underline{v}; \underline{q})|^2} \left\{ \Delta^*(\underline{q}, \underline{v}; \underline{q}) + \int d^3 v' \frac{D(\underline{q}, \underline{v}')}{(\underline{v} - \underline{v}') \cdot \underline{q} - i\epsilon} \right\} \quad (\text{VI-103})$$

But from the definition, VI-43,

$$\Delta^*(\underline{q}, \underline{v}; \underline{q}) \equiv 1 + \int d^3 v' \frac{D(\underline{q}, \underline{v}')}{(\underline{v}' + \underline{v} - \underline{q}) \cdot \underline{q} - i\epsilon} \quad (\text{VI-104})$$

Changing  $\underline{v}' \rightarrow -\underline{v}'' + \underline{q}$  in VI-104 and noting from the definition (VI-37) of  $D$  that

$$D(\underline{q}, -\underline{v}'' + \underline{q}) = -D(\underline{q}, \underline{v}'') \quad (\text{VI-105})$$

we obtain

$$\Delta^*(\underline{q}, \underline{v}; \underline{q}) = 1 - \int d^3 v'' \frac{D(\underline{q}, \underline{v}'')}{(\underline{v} - \underline{v}'') \cdot \underline{q} - i\epsilon} \quad (\text{VI-106})$$

Thus

$$\int P(\underline{q}, \underline{v}) d^3 v = \int d^3 v \frac{Q(\underline{q}, \underline{v})}{|\Delta(\underline{q}, \underline{v}; \underline{q})|^2} \quad (\text{VI-107})$$

and we obtain from VI-96 and VI-97 the desired result:

$$\epsilon_{\text{corr}}(g^2) = \frac{N^2 m^3}{2 \hbar^3} \int_0^{g^2} dg'^2 d^3 q d^3 v f\left(\frac{m}{\hbar} q\right) \frac{Q(\underline{q}, \underline{v}; g'^2)}{|\Delta(\underline{q}, \underline{v}; \underline{q}; g'^2)|^2} \quad (\text{VI-108})$$

where  $\mathcal{Q}$  and  $\Delta$  are defined by VI-38, VI-43 and VI-48, and, for Coulomb interactions,

$$f\left(\frac{m}{\hbar} q\right) = \frac{4\pi\hbar^2}{m^2} \cdot \frac{1}{q^2} \quad (\text{VI-109})$$

The problem is thus formally solved.

We now apply VI-108 to the electron gas at zero temperature. For convenience we deal first with VI-97. Converting to dimensionless variables and using the explicit forms for  $\mathcal{Q}$ ,  $\Delta$  and  $\tilde{F}^{(1)}$  (i.e. the Fermi sphere), we find after a few manipulations that the correlation-interaction energy per particle is given (in Rydbergs) by the expression

$$\begin{aligned} \bar{E}_{\text{int}}^{\text{corr}} \equiv \frac{E_{\text{int}}^{\text{corr}}}{n \left( \frac{me^4}{2\hbar^2} \right)} &= -\frac{3}{4\pi^5} \int_{\substack{|\underline{v}| < 1 \\ |\underline{v}+\underline{q}| > 1}} \frac{d^3 \underline{q}}{q^2} \int_{\substack{|\underline{v}'| < 1 \\ |\underline{v}'+\underline{q}| > 1}} d^3 \underline{v}' \left[ \overbrace{\frac{1}{q^2}}^{\text{direct}} - \overbrace{\frac{1}{2(\underline{q}+\underline{v}+\underline{v}')^2}}^{\text{exchange}} \right] \\ &\times \frac{1}{(\underline{v}+\underline{v}'+\underline{q}) \cdot \underline{q}} \times \left| 1 + \frac{\alpha r_s}{\pi^2 q^2} \int_{\substack{|\underline{v}''| < 1 \\ |\underline{v}''+\underline{q}| > 1}} d^3 \underline{v}'' \left\{ \frac{1}{(\underline{v}''+\underline{v}+\underline{q}) \cdot \underline{q} + i\epsilon} + \frac{1}{(\underline{v}''-\underline{v}) \cdot \underline{q} - i\epsilon} \right\} \right|^{-2} \end{aligned} \quad (\text{VI-110})$$

where

$$\alpha \equiv \left( \frac{4}{9\pi} \right)^{1/3} \quad r_s \equiv \frac{me^2}{\hbar^2} \left( \frac{4\pi}{3n} \right)^{1/3} \quad (\text{VI-111})$$

It is quite interesting to note that VI-110 is precisely twice the result obtained for the total correlation energy per electron in second order perturbation theory\*, with the difference that the "bare" Coulomb interaction

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\*c.f. equations (8) and (9) of Gell-Mann-Brueckner (54).

(both for the direct and exchange terms) is "dressed" by the dynamical (Hartree) dielectric constant.

It is convenient to split VI-110 into three parts: the "direct" contribution ( $\epsilon_a$ ), the exchange contribution ( $\epsilon_b^0$ ) in the high density limit ( $r_s \rightarrow 0$ ), and the additional exchange contribution ( $\Delta\epsilon_b$ ) at non-zero  $r_s$ . Specifically, let

$$\bar{\epsilon}_{int}^{corr} \equiv \epsilon_a + \epsilon_b^0 + \Delta\epsilon_b \quad (VI-112)$$

where (in obvious notation)

$$\epsilon_a \equiv -\frac{3}{4\pi^5} \int \frac{d^3q}{q^2} \int_{|x|<1} d^3r \int_{|x'+q|>1} d^3r' \frac{1}{q^2} \cdot \frac{1}{(\tilde{r}+\tilde{r}'+\tilde{q}) \cdot \tilde{q}} \cdot \frac{1}{|\tilde{r}|^2} \quad (VI-113)$$

$$\epsilon_b^0 \equiv +\frac{3}{8\pi^5} \int \frac{d^3q}{q^2} \int_{|x|<1} d^3r \int_{|x'+q|>1} d^3r' \frac{1}{(\tilde{q}+\tilde{r}+\tilde{r}')^2} \cdot \frac{1}{(\tilde{r}+\tilde{r}'+\tilde{q}) \cdot \tilde{q}} \quad (VI-114)$$

and

$$\Delta\epsilon_b \equiv \frac{3}{8\pi^5} \int \frac{d^3q}{q^2} \int_{|x|<1} d^3r \int_{|x'+q|>1} d^3r' \frac{1}{(\tilde{q}+\tilde{r}+\tilde{r}')^2} \cdot \frac{1}{(\tilde{r}+\tilde{r}'+\tilde{q}) \cdot \tilde{q}} \left( \frac{1}{|\tilde{r}|^2} - 1 \right) \quad (VI-115)$$

We shall now show that  $\epsilon_a$  and  $\epsilon_b^0$  lead (through VI-96) to precisely the correlation energy obtained by G-B.  $\Delta\epsilon_b$ , arising from the screening of the exchange interaction, goes beyond G-B and corresponds to the summation of an infinite series of diagrams less divergent in each order of perturbation theory than those contributing to their result.

Turning first to  $\epsilon_b^0$  since it is just a constant times the Rydberg, it is proportional to  $e^4$ . The integration in VI-96 then brings in a factor



of 1/2 and we find

$$\overline{(\epsilon_{corr})}_b^0 = \frac{3}{16\pi^5} \int_{\frac{|\underline{v}|<1}^{|\underline{v}+\underline{\xi}|>1}} d^3 \underline{q} \int_{\frac{|\underline{v}'|<1}^{|\underline{v}'+\underline{\xi}|>1}} d^3 \underline{v} \int d^3 \underline{v}' \frac{1}{(\underline{q} + \underline{v} + \underline{v}')^2} \frac{1}{(\underline{v} + \underline{v}' + \underline{\xi}) \cdot \underline{q}} \quad (\text{VI-116})$$

This is just what G-B call " $\epsilon_b^{(2)}$ " which they have evaluated by the Monte-Carlo method, with the result

$$\overline{(\epsilon_{corr})}_b^0 = \epsilon_b^{(2)} = 0.046 \pm 0.002 \quad (\text{VI-117})$$

Considerably less manifest is the connection between  $\epsilon_a$  and the remainder of the G-B result. In VI-113, let us introduce the new variables

$$\begin{aligned} \Omega &\equiv \underline{v} \cdot \underline{q} + q^2/2 \\ \Omega' &\equiv \underline{v}' \cdot \underline{q} + q^2/2 \end{aligned} \quad (\text{VI-118})$$

The integrand is then seen to depend only on  $\Omega$ 's and  $q$ . The (strictly geometrical) angular integrations can now be performed. Defining the geometrical factor  $g(\Omega, q)$ :

$$\int_0^\infty g(\Omega, q) d\Omega \equiv \int_{\substack{0 < v < 1 \\ -qv + q^2/2 \leq \Omega \leq qv + q^2/2 \\ \Omega \geq \frac{1-v^2}{2}}} 2\pi v dv \frac{d\Omega}{q} \quad (\text{VI-119})$$

(where the limits of integration have been obtained from  $|\underline{v}| < 1$  and

$|\nu + \frac{1}{2}| > 1$ ), we find that VI-113 becomes

$$\epsilon_a = -\frac{3}{4\pi^5} \cdot 4\pi \int_0^\infty \frac{d\epsilon}{\epsilon^2} \int_0^\infty d\Omega g(\Omega, \epsilon) \left\{ \frac{\int_0^\infty d\Omega' g(\Omega', \epsilon) \frac{1}{\Omega + \Omega'}}{\left| 1 + \frac{\alpha r_s}{\pi^2 \epsilon^2} \int_0^\infty d\Omega'' g(\Omega'', \epsilon) \left( \frac{1}{\Omega + \Omega'' + i\epsilon} + \frac{1}{\Omega'' - \Omega - i\epsilon} \right) \right|^2} \right\}$$

(VI-120)

To proceed, we adopt a method suggested by the paper of Sawada et al (85) wherein the connection between the G-B result and a meson-theoretic treatment of the same problem by Sawada (90) is explored. Specifically, we define the following function of complex  $\Omega$  :

$$f(\Omega, \epsilon) \equiv \frac{\alpha r_s}{\pi^2 \epsilon^2} \int_0^\infty g(\Omega', \epsilon) \left[ \frac{1}{\Omega' + \Omega} + \frac{1}{\Omega' - \Omega} \right] d\Omega'$$

(VI-121)

Its analytic properties are readily established from the definition VI-119: for  $\epsilon \leq 2$ , it has a single branch cut from  $(-\epsilon - \epsilon^2/2)$  to  $(\epsilon + \epsilon^2/2)$ ; for  $\epsilon > 2$ , the cut splits into two parts, one extending from  $(-\epsilon - \epsilon^2/2)$  to  $(-\epsilon^2/2 + \epsilon)$  and the other from  $(\epsilon^2/2 - \epsilon)$  to  $(\epsilon^2/2 + \epsilon)$ .

Now from VI-121 and the theorem VI-46, one readily establishes the relation

$$g(\Omega, \epsilon) = \frac{\pi^2 \epsilon^2}{\pi \alpha r_s} \cdot \frac{1}{2i} \cdot (f(\Omega + i\epsilon) - f(\Omega - i\epsilon)) \quad (VI-122)$$

where use has been made of the fact\* that

$$g(-\Omega, \epsilon) = 0 \quad (VI-123)$$

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\*This relation does not hold at non-zero temperatures.

Then, from VI-120, VI-121, and the identity

$$\left( \frac{1}{1+f(\Omega+i\epsilon)} \right) \left( \frac{1}{1+f(\Omega-i\epsilon)} \right) \equiv \frac{1}{[f(\Omega+i\epsilon) - f(\Omega-i\epsilon)]} \left[ \frac{f(\Omega+i\epsilon)}{1+f(\Omega+i\epsilon)} - \frac{f(\Omega-i\epsilon)}{1+f(\Omega-i\epsilon)} \right] \quad (\text{VI-124})$$

we find that VI-120 becomes

$$\epsilon_a = \frac{-3}{4\pi^5} \cdot 4\pi \cdot \frac{\pi^2}{\pi^2 r_s} \cdot \frac{1}{2i} \int_0^\infty d\Omega \int_0^\infty d\Omega' \left[ \frac{f(\Omega+i\epsilon)}{1+f(\Omega+i\epsilon)} - \frac{f(\Omega-i\epsilon)}{1+f(\Omega-i\epsilon)} \right] \int_0^\infty \frac{g(\Omega', \eta) d\Omega'}{\Omega + \Omega'} \quad (\text{VI-125})$$

If we now define another function of complex  $\Omega$  :

$$h(\Omega, \eta) \equiv \int_0^\infty g(\Omega', \eta) \frac{d\Omega'}{\Omega + \Omega'} \quad (\text{VI-126})$$

and note that

$$h(\Omega, \eta) = h(\Omega \pm i\epsilon, \eta) \quad \text{if } \text{Re } \Omega \geq 0 \quad (\text{VI-127})$$

then

$$\int_0^\infty d\Omega \left[ \frac{f(\Omega+i\epsilon)}{1+f(\Omega+i\epsilon)} - \frac{f(\Omega-i\epsilon)}{1+f(\Omega-i\epsilon)} \right] \int_0^\infty \frac{g(\Omega', \eta) d\Omega'}{\Omega + \Omega'} = \int_{0+i\epsilon}^{\infty+i\epsilon} - \int_{0-i\epsilon}^{\infty-i\epsilon} \left[ \frac{f(\Omega)}{1+f(\Omega)} h(\Omega) \right] d\Omega \quad (\text{VI-128})$$

In order to write the r.h.s. of VI-128 as a contour integral, we must explore the analytic properties of the integrand in the right half plane. Since  $h$  is analytic there, the integrand has the branch cut of  $f$  cited earlier and a (possible) pole at the zero of  $1+f$ . Now  $(1+f)$  is the R.P.A. dielectric constant whose analytic properties are well known (95).



For small  $q$ ,  $(1+f)^{-1}$  has a legitimate pole at the real plasmon frequency  $\Omega_{pe}(q)$ . For  $q > q_{max}$ , however, where

$$q_{max}^2 \equiv \frac{\alpha r_s}{\pi} \left[ (2 + q_{max}) \ln \left( 1 + \frac{2}{q_{max}} \right) - 2 \right] \quad (VI-129)$$

the zero of  $(1+f)$  enters the branch cut and hence ceases to be a true pole. In any event, since  $\Omega_{pe}(q=0)$  is finite, we can for any  $q$  write VI-128 as

$$\int_{C_1} \frac{f(\Omega) h(\Omega)}{1+f(\Omega)} d\Omega \quad (VI-130)$$

where the contour  $C_1$  is defined in fig. 1.

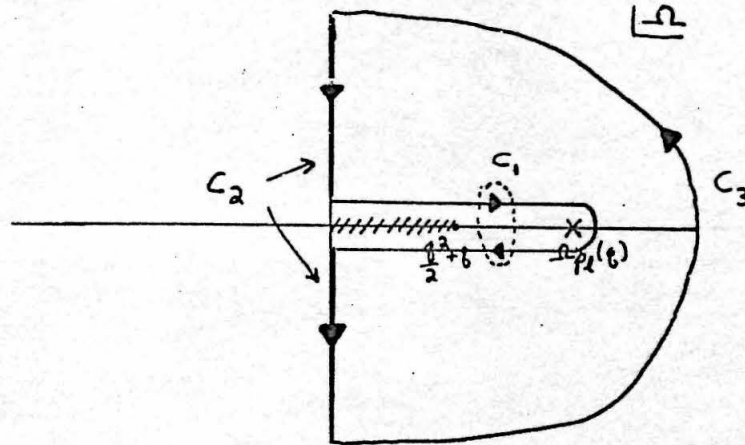


Figure 1: Contours for evaluation of VI-128

Closing the contour as indicated in the figure, and noting from the known properties of  $f$  that the contribution from  $C_3$  vanishes, we obtain

$$\int_{C_1} \frac{fh}{1+f} d\Omega = - \int_{C_2} \frac{fh}{1+f} d\Omega = \int_{-i\infty}^{+i\infty} \frac{fh}{1+f} d\Omega = i \int_{-\infty}^{\infty} \frac{f(i\zeta, q) h(i\zeta, q)}{1+f(i\zeta, q)} d\zeta$$

All that now remains is thus to explore the analytic continuation of  $h$  to the imaginary axis. Note first from the definition of  $f$  that

$$f(-\Omega) = f(\Omega) \quad (\text{VI-132})$$

Then

$$\int_{-\infty}^{\infty} \frac{f(i\tau, \eta) h(i\tau, \eta) d\tau}{1 + f(i\tau, \eta)} = \int_0^{\infty} \frac{f(i\tau, \eta)}{1 + f(i\tau, \eta)} [h(i\tau, \eta) + h(-i\tau, \eta)] d\tau \quad (\text{VI-133})$$

But from VI-126 and VI-122,

$$h(i\tau, \eta) + h(-i\tau, \eta) = \frac{\pi^2 \eta^2}{\pi \alpha r_s} \cdot \frac{1}{2i} \cdot \int_0^{\infty} [f(\Omega' + i\epsilon) - f(\Omega' - i\epsilon)] \left[ \frac{1}{\Omega' + i\tau} + \frac{1}{\Omega' - i\tau} \right] d\Omega' \quad (\text{VI-134})$$

which, by virtue of the symmetry of the integrand under the interchange

$\Omega' \rightarrow -\Omega'$ , can be written

$$h(i\tau, \eta) + h(-i\tau, \eta) = \frac{\pi^2 \eta^2}{\pi \alpha r_s} \cdot \frac{1}{2i} \cdot \frac{1}{2} \int_{-\infty}^{\infty} [f(\Omega' + i\epsilon) - f(\Omega' - i\epsilon)] \left[ \frac{1}{\Omega' + i\tau} + \frac{1}{\Omega' - i\tau} \right] d\Omega' \quad (\text{VI-135})$$

VI-135 is now expressible as a contour integral:

$$h(i\tau, \eta) + h(-i\tau, \eta) = \frac{\pi^2 \eta^2}{\pi \alpha r_s} \cdot \frac{1}{2i} \cdot \frac{1}{2} \int_{C_1} + \int_{C_2} d\Omega' f(\Omega') \left[ \frac{1}{\Omega' + i\tau} + \frac{1}{\Omega' - i\tau} \right] \quad (\text{VI-136})$$

as indicated in figure 2.

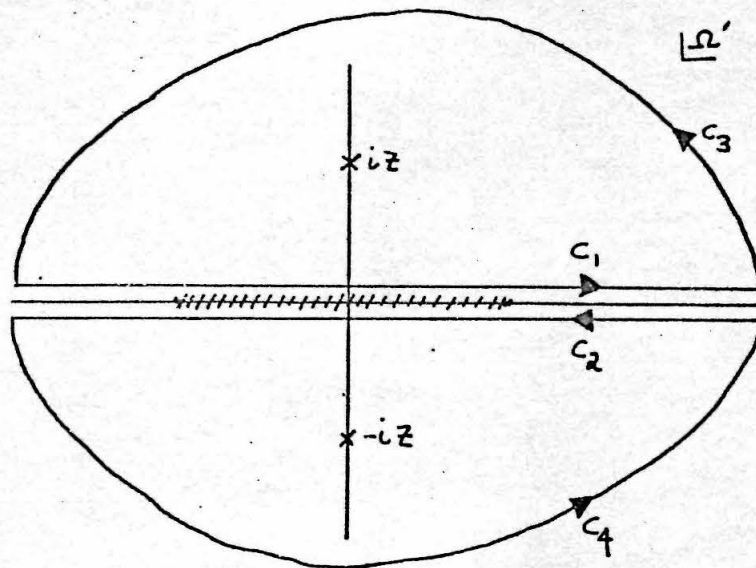


Figure 2: Contours for evaluation of VI-136

Closing the contours and evaluating the residues leads to the desired result

$$h(iz, q) + h(-iz, q) = \frac{\pi^2 q^2}{\alpha r_s} f(iz) \quad (\text{VI-137})$$

where use has been made of VI-132.

Combining VI-137, VI-133, VI-128 and VI-125 gives

$$\epsilon_a = -\frac{3}{4\pi\alpha^2 r_s^2} \int_0^\infty dq q^2 \int_{-\infty}^\infty \frac{f^2(iz, q)}{1+f(iz, q)} dz = -\frac{3}{4\pi\alpha^2 r_s^2} \int_0^\infty dq q^3 \int_{-\infty}^\infty \frac{f^2(iuq, q)}{1+f(iuq, q)} du \quad (\text{VI-138})$$

$u \equiv \frac{z}{q}$

The function  $f$  is easily shown from VI-121 and VI-119 to be connected to the function  $Q_q(u)$  defined by G-F (eq. 18) via:

$$f(iuq, q) = \frac{\alpha r_s}{\pi^2 q^2} Q_q(u) \quad (\text{VI-139})$$



Inserting VI-139 into VI-138 and doing the integral over the coupling constant leads to the final result

$$(\overline{\epsilon_{\text{corr}}})_a = \frac{3}{4\pi\alpha^2 r_s^2} \int_0^\infty d\eta \eta^3 \int_{-\infty}^\infty \left[ \ln \left( 1 + \frac{\alpha r_s}{\pi^2 \eta^2} Q_\eta(u) \right) - \frac{\alpha r_s}{\pi^2 \eta^2} Q_\eta(u) \right] du \quad (\text{VI-140})$$

which is identical to the result obtained by G-B in series form (equation (19) in G-B). VI-140 has been evaluated numerically by G-B in the high density limit and they find

$$(\overline{\epsilon_{\text{corr}}})_{\text{G-B}} = (\overline{\epsilon_{\text{corr}}})_a + (\overline{\epsilon_{\text{corr}}})_b^0 = 0.0622 \ln r_s - 0.096 + O(r_s \ln r_s) \frac{\text{Ryd}}{\text{electron}} \quad (\text{VI-141})$$

Going beyond G-B, we now evaluate the leading contribution to the correlation energy in the high density limit arising from VI-115. Doing the coupling constant integration first, we obtain

$$(\overline{\epsilon_{\text{corr}}})_{\Delta b} = \frac{-3}{8\pi^5} \int \frac{d^3 q}{q^2} \int_{|u|<1} d^3 u \int_{|u'|<1} d^3 u' \frac{1}{(q+u+u')^2} \frac{1}{q \cdot (q+u+u')} \\ \times \left\{ \frac{1}{2} + \frac{1}{f-f^*} \left( \frac{1}{f} \ln(1+f) - \frac{1}{f^*} \ln(1+f^*) \right) \right\} \quad (\text{VI-142})$$

$|u+q|>1 \quad |u'+q|>1$

where

$$f \equiv \frac{\alpha r_s}{\pi^2 q^2} \int_{|u''|<1} d^3 u'' \left( \frac{1}{(u''+u+q) \cdot q + i\epsilon} + \frac{1}{(u''-u) \cdot q - i\epsilon} \right) \quad (\text{VI-143})$$

$|u''+q|>1$

Expanding the term in curly brackets about  $r_s = 0$ , we obtain in lowest order

$$\begin{aligned}
 (\overline{\epsilon_{\text{corr}}})_{\Delta b} \cong & -\frac{1}{4\pi^5} \left[ \int \frac{d^3 q}{q^4} \int_{|v|<1} d^3 v \int_{|v'|<1} d^3 v' \frac{1}{(\underline{q} + \underline{v} + \underline{v}')^2} \frac{1}{\underline{q} \cdot (\underline{q} + \underline{v} + \underline{v}')} \right. \\
 & \left. \times \int_{|v''|<1} d^3 v'' \left( \frac{1}{(\underline{v}'' + \underline{v} + \underline{q}) \cdot \underline{q}} + \frac{1}{(\underline{v}'' - \underline{v}) \cdot \underline{q}} \right) \right] \frac{\alpha r_s}{\pi^2} \quad (VI-144) \\
 & |v'' + \underline{q}| > 1
 \end{aligned}$$

The integral diverges logarithmically at small  $q$ . As is evident from the work of G-B, however, retention of the full VI-142 effectively screens the Coulomb interaction at large distances -- tantamount to cutting off the  $q$  integration for  $q < q_{\min} \sim (\text{const.}) r_s^{1/2}$ . Thus, proceeding analogously to G-B, all we need do is find the strength of the logarithmic divergence of VI-144. We can therefore expand everything in VI-144 for small  $q$  and retain only the leading terms. After some straightforward algebra, we first obtain

$$(\overline{\epsilon_{\text{corr}}})_{\Delta b} = -\frac{2\alpha r_s}{\pi^4} \left[ \int_{q_{\min} \sim r_s^{1/2}} \frac{d^3 q}{q} \int_0^1 dp p \int_0^1 dp' p' \int_0^{2\pi} d\phi' \frac{1}{1 + \hat{\underline{q}} \cdot \hat{\underline{v}}'} \frac{1}{p + p'} \left[ 2 - \frac{1}{p} \ln \left( \frac{1+p}{1-p} \right) \right] \right] \quad (VI-145)$$

which displays the logarithmic divergence. Taking its strength and performing the  $p'$  and  $\phi'$  integrations yields

$$\begin{aligned}
 (\overline{\epsilon_{\text{corr}}})_{\Delta b} &= \frac{\alpha r_s \ln r_s}{\pi^4} \left\{ 2\pi \int_0^1 dp p \left[ 2 - \frac{1}{p} \ln \left( \frac{1+p}{1-p} \right) \right] \left[ \ln \left( \frac{1+p}{p} \right) - \frac{1}{1+p} \right] \right\} \\
 &\equiv \frac{\alpha r_s \ln r_s}{\pi^4} A \quad (VI-146)
 \end{aligned}$$

The integrals contributing to A could all be done analytically, with the exception of

$$\int_0^1 dp \ln(1-p) \left[ \frac{1}{1+p} - \ln(1+p) \right] \approx \ln 2 - 0.696 \quad (\text{VI-147})$$

which was numerically evaluated by means of a rapidly convergent series.

We obtain for A

$$A = -28.4 \quad (\text{VI-148})$$

and thus

$$(\bar{E}_{\text{corr}})_{\Delta b} = -0.151 r_s \ln r_s \text{ Ryd/electron} \quad (\text{VI-149})$$

VI-149 is in marked disagreement with what is apparently\* the only other calculation of this quantity -- that of DuBois (92). He obtained the numerical value ( - .00045) for the coefficient of  $(r_s \ln r_s)$  which is two to three orders of magnitude smaller than ours. While the actual numerical value of this coefficient is of little (if any) practical value, the discrepancy, if real, would be indicative of the inadequacy of VI-108 beyond the high density limit. We can offer a few reasons to doubt the plausibility of DuBois' value. First, the coefficient of the "direct"  $r_s \ln r_s$  term (obtained from VI-140) was found by Dubois to be + .0052, a value ten times larger than the exchange term, in marked contrast to Hubbard's (93) estimate that exchange should play a quite significant role. Second, the value given by DuBois is two orders of magnitude smaller than the exchange contribution to the constant term in the correlation energy (i.e.  $\epsilon_b^{(2)}$ ). It is difficult to imagine that Nature is so convergent. In any event, the discrepancy

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\*D. Dubois (private communication). Dr. Dubois also indicated that his numerical value has never been fully checked although he has the fullest confidence in the analytic expression from which it was obtained.



has not been at all explored as it certainly must ultimately be. For if we are actually in agreement, this would offer a strong motivation to numerically evaluate VI-108 at metallic densities.

In sum, if we adopt DuBois' value for the "direct"  $r_s \ln r_s$  term, we obtain

$$\bar{E}_{\text{corr}} = 0.0622 \ln r_s - 0.096 - 0.146 r_s \ln r_s + O(r_s) \quad \text{Ryd/electron} \quad (\text{VI-150})$$

as compared to his net result

$$\bar{E}_{\text{corr}} = 0.0622 \ln r_s - 0.096 + 0.0047 r_s \ln r_s + O(r_s) \quad \text{Ryd/electron} \quad (\text{VI-151})$$

We conclude this chapter with a speculation occasioned by VI-99. Since  $E_{\text{int}}^{\text{corr}}$  as given by VI-97 and VI-107 is in the form of an integral over  $\mathcal{V}$  space, we can formally rewrite VI-99 as

$$E_{\text{kin}}^{\text{corr}}(g^2) = \int d^3v \frac{1}{2} m v^2 \left\{ \frac{1}{\frac{1}{2} m v^2} \frac{N^2 m^3}{2 \hbar^3} \int d^3q f\left(\frac{m}{\hbar} q\right) \right. \\ \left. \times \left[ \int_0^{g^2} \frac{Q(\underline{q}, \underline{v}; g'^2)}{|\Delta(\underline{q}, \underline{v}; \underline{q}, g'^2)|^2} dg'^2 - g^2 \frac{Q(\underline{q}, \underline{v}; g^2)}{|\Delta(\underline{q}, \underline{v}; \underline{q}, g^2)|^2} \right] \right\} \quad (\text{VI-152})$$

But, by definition,

$$E_{\text{kin}}^{\text{corr}}(g^2) \equiv \int d^3v \left( \frac{1}{2} m v^2 \right) \left\{ (N \Delta \tilde{F}_{\text{corr}}^{(1)}(g^2)) \right\} \quad (\text{VI-153})$$

where  $\Delta_{\text{corr}} \tilde{f}^{(n)}$  is the change in  $\tilde{f}^{(n)}$  due to correlations. It is therefore quite tempting to identify the two curly brackets with each other although, of course, there is no logical necessity to do so. If true, this would be a trivial method for evaluating the "smearing out" of the Fermi surface, at least to lowest order. Thus, inserting the specific form VI-38 for  $Q$ , and converting to the usual dimensionless variables, we are led to the conjecture:

$$\begin{aligned} \Delta_{\text{corr}} \tilde{f}^{(n)} &\stackrel{?}{=} \frac{e^4}{2k^2 v_f^2 \pi^4} \frac{1}{v^2} \int \frac{d^3 q}{q^2} \left\{ \tilde{f}^{(n)}(\underline{v} + \underline{q}) [1 - \tilde{f}^{(n)}(\underline{v})] \int \frac{d^3 v' \tilde{f}^{(n)}(\underline{v}' + \underline{q}) [1 - \tilde{f}^{(n)}(\underline{v}')] }{(\underline{v} + \underline{v}' + \underline{q}) \cdot \underline{q}} \right. \\ &\times \left[ \frac{1}{q^2} - \frac{1}{2(\underline{v} + \underline{v}' + \underline{q})^2} \right] - \tilde{f}^{(n)}(\underline{v}) [1 - \tilde{f}^{(n)}(\underline{v} + \underline{q})] \int \frac{d^3 v' \tilde{f}^{(n)}(\underline{v}') [1 - \tilde{f}^{(n)}(\underline{v}' + \underline{q})] }{(\underline{v} + \underline{v}' + \underline{q}) \cdot \underline{q}} \\ &\times \left[ \frac{1}{q^2} - \frac{1}{2(\underline{v} + \underline{v}' + \underline{q})^2} \right] \Bigg\} \times \left\{ \frac{1}{r_s^2} \int_0^{r_s} r_s' dr_s' \left| 1 + \frac{\alpha r_s'}{\pi^2 q^2} \int d^3 v'' \tilde{f}^{(n)}(\underline{v}'') [1 - \tilde{f}^{(n)}(\underline{v}'' + \underline{q})] \right. \right. \\ &\times \left. \left[ \frac{1}{(\underline{v}'' + \underline{v} + \underline{q}) \cdot \underline{q} + i\epsilon} + \frac{1}{(\underline{v}'' - \underline{v}) \cdot \underline{q} - i\epsilon} \right] \right\}^2 - \left| \frac{1}{r_s} \right|^{-2} \Bigg\} \quad (\text{VI-154}) \end{aligned}$$

Chapter VII

Summary and Conclusions

Our original motivations for undertaking the present study were twofold. First, to formulate the quantum theory of many-body systems in a fashion which bears maximum resemblance to the corresponding classical theory, and second, to explore the utility and limitations of such a formulation.

In the first of these aims, we have been generally successful. The discovery that the classical and quantum problems can be unified via the Generalized Poisson Bracket, together with conveniently formulated subsidiary conditions on the phase space distribution function as demanded by the symmetry properties of the wave function under particle exchange, has, we feel, a certain formal elegance and conceptual simplicity. The particular circumstance that the Hartree-Fock theory can be rewritten in the form of a simple generalization of the Vlasov equation is especially appealing in view of the analytical complexity introduced by exchange in many other approaches to the problem.

Elegance and simplicity, however, are naturally a question of taste, and the value of the present formulation depends, in the final analysis, on what it enables us to calculate and with how much effort. For this reason, we have included many results (e.g., the exchange-corrected plasmon dispersion relation, spin-waves, the non-zero temperature electron gas in the Hartree-Fock approximation, etc.) which are admittedly not new but which serve to give some indication of the applicability and scope of the method.



There is certainly no doubt that our formalism is particularly applicable to the problem of correcting the classical many-body theory for lowest order quantum and exchange effects, as has been demonstrated, for example, in our treatment of hydrodynamic transport. In the study of the many-electron atom, we have been able to both resolve the problem of the theoretical foundations of the statistical model, and derive its many corrections in a detailed and systematic fashion. We have also indicated the manner in which the last remaining corrections, due to relativity and correlations, can be calculated, after which this unduly overworked subject could be properly laid to rest. Furthermore, the recognition that the success of the statistical model is indicative of the fact that the atom behaves in many ways like a classical inhomogeneous plasma obeying Fermi statistics, has led us to anticipate the existence of collective collisionless modes of excitation.

That our approach should, after all, be convenient in the description of quasi-classical systems is, of course, no surprise due to the manifest ease with which the correspondence limit of the theory can be taken. What we have failed to achieve, however, is a thorough understanding of what classes of many-body systems cannot be fruitfully approached. With the exception of low temperature Bose systems where a possibly trivial modification of the formalism has been shown to be required, it appears that any reasonably homogeneous quantum system in which dynamical correlations between more than two particles can effectively be ignored, should be amenable to a q. m. d. f. approach.

Even at the opposite extreme of a system so strongly correlated that it exhibits liquid-like behavior, the quantum hydrodynamical theory which we have developed should be of value in studying its transport properties.

Particularly gratifying has been our apparent success in computing the correlation energy of the free electron gas, a problem which had hitherto been the exclusive province of the field theorist. It should be recalled that the energy could be written down immediately, once the pair correlation function had been obtained. The only analytical complexity arose in establishing the connection between our work and that of the G-B. Further Study of the apparent discrepancy with DuBois' extension of the G-B result is clearly required, however, before we can confidently hope to apply our expression at metallic densities. A calculation of the low temperature specific heat of the electron gas would also be of significant value since approximate experimental and theoretical (94) results at these densities are available.

Perhaps our most significant result, however, is the collision integral derived in VI-C. Recalling that the collision integral is the starting point for an exact kinetic theory of gases, we are now in a position to correct such theories for quantum and exchange effects. Correlation corrections to the theory of plasma oscillations, and the calculation of the effect of exchange on hydrodynamical transport coefficients come immediately to mind as possible applications.

One might also hope to obtain a better understanding of transport processes in the degenerate electron gas by means of an improved equation of state as derived from the pair correlation function together with a hydrodynamic analysis based on the collision integral. Lattice effects can probably be introduced in a relatively straightforward fashion. Of particular interest is whether the low temperature anomaly in the propagation of sound in the electron gas, as found in Chapter IV, persists in the more exact treatment. This is but one of the (unfortunately many) loose ends which have arisen in the present study and which, due to obvious limitations, we have not been able to fully explore. We have tried, however, to call attention to them as they arose and hope that the present formalism will aid in their resolution.



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## Plasma Theory of the Many-Electron Atom

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A new approach to the many electron atom, based on the formal equivalence between the Hartree-Fock equations and a quantum-mechanical generalization of the collisionless Boltzmann (Vlasov) equation, is presented. This equivalence casts the problem into the framework of conventional plasma theory, the Vlasov equation being merely replaced by its quantum-mechanical analog. The quantum Vlasov equation permits a straightforward expansion of the quantum-mechanical phase space distribution function in powers of  $\hbar$ . The first step of this expansion, corresponding physically to a classical correlationless plasma obeying Fermi statistics, leads to the Thomas-Fermi model. Successive steps generate quantum and exchange corrections. The method is applied to the case of the "statistical" correlationless atom (or ion), generalized for the first time to arbitrary temperature and nonzero total orbital angular momentum, with quantum and exchange effects being included to order  $\hbar^2$ .

## I. INTRODUCTION

THE Thomas-Fermi statistical model<sup>1</sup> provides an approximate description of a broad class of spatially inhomogeneous polyelectronic systems, with a degree of success which is surprising in view of its analytical and conceptual simplicity. Attempts to understand this success as well as to improve the model by remedying some of its more obvious shortcomings, have led naturally to investigations of its theoretical foundations.

The first step in this direction was taken by Dirac<sup>2</sup> who, realizing that the Thomas-Fermi model represents in some sense a classical limit of the Hartree-Fock<sup>3</sup> theory, rewrote the Hartree-Fock equations in terms of the density matrix, and succeeded thereby in augmenting the Thomas-Fermi model to approximately take account of electron exchange. Subsequent investigations<sup>4</sup> have generally followed Dirac's lead, in the sense that quasi-classical approximations to the density matrix are studied. In particular, systematic expansions in  $\hbar$  have been developed which lead both to exchange and so-called "inhomogeneity" corrections.

These approaches, however, suffer from two drawbacks: (1) Since they are rooted in the Hartree-Fock approximation, correlation effects are excluded; and (2) the conceptual simplicity of the Thomas-Fermi model is destroyed, with the consequence that while the ordinary Thomas-Fermi model can be trivially general-

ized, for example, to arbitrary temperatures<sup>5</sup> or nonzero total orbital angular momenta,<sup>6</sup> the procedure for systematically obtaining quantum and exchange corrections in these cases is somewhat obscure.

Recently, an attempt to remedy the former of these difficulties by supplanting the density matrix formalism with the more powerful techniques of field theory has been reported.<sup>7</sup> While such methods hold promise for progress on the correlation question, they unfortunately lead to an aggravation of the second difficulty, since they are based on a formulation of quantum statistical mechanics which is even further conceptually removed from the traditional statistical approach underlying the Thomas-Fermi model than is the density matrix.

In the present paper, therefore, we step in the opposite direction and attempt to establish maximal contact with conventional statistical mechanics by dealing directly with a quantum-mechanical generalization of the phase space density, which turns out, in fact, to be essentially the Fourier transform of the density matrix. This difference, although apparently trivial from a formal standpoint, enables us to cast the problem entirely into the familiar charged-particle statistical mechanics, or "plasma" theory. As a consequence, difficulty (2) vanishes and, although we do not concern ourselves here with (1), i.e., the inclusion of correlation, a close connection between this problem and contemporary difficulties in plasma physics emerges.

Our method is best introduced by briefly outlining the traditional statistical approach to the problem of  $N$  identical particles which interact both mutually and with a fixed oppositely charged "nucleus" via their instantaneous Coulomb forces. One begins with the  $6N$  dimensional phase space distribution function,

<sup>1</sup>The most recent comprehensive review articles dealing with the Thomas-Fermi model are those of P. Gombas in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 36; and N. H. March, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1957), Vol. 6, p. 1.

<sup>2</sup>P. A. M. Dirac, *Proc. Cambridge Phil. Soc.* 26, 376 (1930).

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<sup>5</sup>T. Sakai, *Proc. Phys. Math. Soc. Japan* 24, 254 (1942); R. P. Feynman, N. Metropolis, and E. Teller, *Phys. Rev.* 75, 1561 (1949).

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<sup>7</sup>G. A. Baraff and S. Borowitz, *Phys. Rev.* 121, 1704 (1961).



$F_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N; t)$  whose dynamical (Liouville) equation is obtained from the Newtonian equations of motion. Singlet, doublet, etc., distribution functions are then defined as the integral of  $F_N$  over  $N-1$ ,  $N-2$ , etc., dimensional phase subspaces. The (coupled) dynamical equations for these quantities, the so-called BBGKY<sup>8</sup> hierarchy, are obtained by integrating the Liouville equation over appropriate phase subspaces. To proceed further, this system of equations is approximated by truncating the chain at some point. The simplest such approximation is to assume that the doublet distribution is given simply by the product of singlet functions, corresponding to the neglect of all correlations, or "collisions." As is well known,<sup>9</sup> this procedure leads to the "collisionless" Boltzmann, or Vlasov<sup>10</sup> equation for the singlet distribution function,  $F_1(\mathbf{r}, \mathbf{p}, t)$ . The Vlasov equation is satisfied identically by the set  $\{F_i\}$  of functionals of the constants of the motion of a single particle in the average field of all the others. The neglect of collisions is then approximately remedied by the *ansatz* that their effect is to single out that member of  $\{F_i\}$  which maximizes the entropy, subject to the constraints on the total system (i.e., total energy, number of particles, angular momentum, etc.). (To the extent that only two body collisions are important, this procedure is validated by the *H* theorem.) Higher approximations, corresponding to a more exact treatment of correlations, lead to formidable analytical difficulties which are currently being attacked on various fronts.<sup>11</sup>

The question now arises as to how this procedure is to be quantum-mechanically generalized. The simplest generalization is to merely introduce the appropriate quantum statistics into the entropy maximization. This, we find, leads to the Thomas-Fermi model (with Fermi-Amaldi<sup>12</sup> correction). It is clear, however, that the Vlasov equation must also be quantum-mechanically augmented. This has been done by one of us<sup>13</sup> in a previous paper along lines analogous to the derivation of the Vlasov equation sketched above. A quantum-mechanical phase space distribution function (q.m.d.f.),  $\tilde{F}_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N; \mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N; t)$ , is defined which approaches the classical distribution function as  $\hbar \rightarrow 0$ . The quantum analog of the Liouville equation for  $\tilde{F}_N$  is then obtained from the Schrödinger equation for the  $N$ -particle wave function,  $\psi_N$ . Decomposition of  $F_N$  into singlet, doublet, etc., functions leads to the quantum counterpart of the BBGKY chain, which is then truncated, as before, by neglecting correlations. This truncation is equivalent to replacing  $\psi_N$  by a single

Slater determinant, so that the quantum Vlasov equation thus obtained is formally equivalent to the Hartree-Fock equations. The resulting partial differential equation for the singlet q.m.d.f.,  $\tilde{F}$ , is introduced in Sec. II. It has the convenient property of permitting a straightforward expansion of  $\tilde{F}$  in powers of  $\hbar$ , thereby unambiguously generating quantum and exchange corrections from the zeroth-order (Thomas-Fermi) solution.

We illustrate this method by considering an atom (or ion) at arbitrary temperature, with nonzero total orbital angular momentum. In Sec. III, the Thomas-Fermi model for this case is derived from the Vlasov equation along the lines sketched above. The quantum and exchange corrections to order  $\hbar^2$  are then obtained from the quantum Vlasov equation in Sec. IV. In the limit of zero temperature and zero orbital angular momentum, our result agrees with that obtained by others<sup>1</sup> via the density matrix. In the concluding section, we briefly re-examine the correlation question from the plasma-theoretic point of view developed in this paper.

## II. QUANTUM VLASOV EQUATION

The quantum Vlasov equation has been derived by one of us in a previous paper,<sup>13</sup> where it was written in a form facilitating its application to the study of quantum corrected longitudinal plasma oscillations. Since in the present paper we shall be dealing with  $N$  electrons (mass  $m$ , charge  $-|e|$ ) in the field of a fixed point nucleus (charge  $+Z|e|$ ), rather than the extended homogeneous plasma considered previously, a few trivial modifications are required: (i) the elimination of the action of an electron on itself; (ii) appropriate spin space averaging of the exchange term.<sup>14</sup> The resulting equation for the singlet q.m.d.f.,  $\tilde{F}(\mathbf{r}, \mathbf{v}, t)$ , can be written as

$$\begin{aligned} & \left( \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} - \frac{1}{m} \nabla_{\mathbf{r}} U \cdot \nabla_{\mathbf{v}} \right) \tilde{F} \\ &= \frac{i\hbar}{2m} \left\{ \nabla_{\mathbf{r}}^2 \tilde{F} - \frac{1}{m} \sum_{n=0}^{\infty} \left( \frac{-i\hbar}{m} \right)^n \frac{2}{(n+2)!} (\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{v}})^{n+2} U \tilde{F} \right\} \\ &+ \frac{ie^2 \hbar}{2m^2} \frac{N-1}{N} \int d^3l \exp(i\mathbf{l} \cdot \mathbf{v}) \tilde{f}(\mathbf{r}, \mathbf{l}, t) \\ &\times \left\{ \frac{1}{l} \tilde{F} \left( \mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}, t \right) - \frac{1}{2\pi^2} \int \frac{d^3v'}{|\mathbf{v} - \mathbf{v}'|^2} \right. \\ &\quad \left. \times \tilde{F} \left( \mathbf{r} + \frac{\hbar}{m} \mathbf{l}, \mathbf{v}', t \right) \right\}, \quad (1) \end{aligned}$$

<sup>8</sup> A set of equations derived independently by N. N. Bogolubov, M. Born, H. S. Green, J. G. Kirkwood, and J. Yvon.

<sup>9</sup> M. Rosenbluth and N. Rostoker, *Phys. Fluids* **3**, 1 (1960).

<sup>10</sup> A. Vlasov, *J. Phys. (USSR)* **9**, 25 (1945).

<sup>11</sup> B. D. Fried and H. W. Wyld, Jr., *Phys. Rev.* **122**, 1 (1961).

<sup>12</sup> E. Fermi and E. Amaldi, *Mem. acad. Italia* **6**, 117 (1934).

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where

$$\nabla^2 U = -4\pi e^2 \frac{N-1}{N} \int d^3v \bar{F}(\mathbf{r}, \mathbf{v}, t), \quad (2)$$

$$\lim_{r \rightarrow 0} U = -\frac{Ze^2}{r}, \quad U \sim_{r \rightarrow \infty} \frac{(Z-N+1)e^2}{r}, \quad (3)$$

$$\bar{F}(\mathbf{r}, \mathbf{v}, t) = (2\pi)^{-3} \int d^3l \hat{f}(\mathbf{r}, \mathbf{l}, t) \exp(i\mathbf{l} \cdot \mathbf{v}), \quad (4)$$

$$(\nabla_r \cdot \nabla_v)^n U \bar{F} \equiv \frac{\partial^n U}{\partial x_i \partial x_j \dots} \frac{\partial^n \bar{F}}{\partial v_i \partial v_j \dots}, \quad (5)$$

( $i, j, \dots$  are Cartesian indices running from 1 to 3)

$$\int \int d^3r d^3v \bar{F}(\mathbf{r}, \mathbf{v}, t) = N, \quad (6)$$

Gaussian units and the convention that repeated indices are to be summed are used throughout. Information is obtained from  $\bar{F}$  (a nonobservable) by integration over configuration and velocity space, i.e., if  $G(\mathbf{r}, \mathbf{v})$  is any function of  $\mathbf{r}$  and  $\mathbf{v}$ , then

$$\int G(\mathbf{r}, \mathbf{v}) \bar{F}(\mathbf{r}, \mathbf{v}, t) d^3r d^3v = \langle \psi(t) | \mathcal{G} | \psi(t) \rangle, \quad (7)$$

where  $\mathcal{G}$  is the operator obtained by well-ordering  $G(\mathbf{r}, \hbar \nabla_r / im)$ , and  $\psi(\mathbf{r}, t)$  is the single-particle Hartree-Fock wave function for the system. Consequently, the quantum-mechanical expectation value of the electron number density  $\rho(\mathbf{r}, t)$  and kinetic energy  $K(t)$  of the system, for example, are given by

$$\rho(\mathbf{r}, t) = \int \bar{F}(\mathbf{r}, \mathbf{v}, t) d^3v, \quad (8)$$

and

$$K(t) = \int \int \left[ \frac{1}{2} m v^2 \right] \bar{F}(\mathbf{r}, \mathbf{v}, t) d^3r d^3v. \quad (9)$$

Since we shall be interested only in the ground state of the system, the time dependence of the above equations will henceforth be suppressed. Consideration of time dependent effects (e.g., collective oscillations) will appear in subsequent papers.

The left-hand side of Eq. (1) is the usual Vlasov operator acting on  $\bar{F}$ . The first term on the right will generate quantum ("inhomogeneity") corrections, while the second term represents the effect of exchange.

#### Expansion in $\hbar$

Equations (1)–(3) are conveniently solved by the following iterative expansion in  $\hbar$ : First, in Eq. (1),

$U$  is assumed to be given, and the expansion

$$\bar{F} = \sum_{n=0}^{\infty} \hbar^n F_n \quad (10)$$

is introduced.  $\bar{F}(\mathbf{r} + \hbar \mathbf{l} / m, \mathbf{v})$ , appearing in the exchange term of (1), is expanded in a Taylor series:

$$\bar{F}(\mathbf{r} + \hbar \mathbf{l} / m, \mathbf{v}) = \bar{F}(\mathbf{r}, \mathbf{v}) + (\hbar \mathbf{l} / m) \cdot \nabla_r \bar{F}(\mathbf{r}, \mathbf{v}) + \dots \quad (11)$$

Introducing (10) and (11) into (1) and equating coefficients of similar powers of  $\hbar$  leads to the following chain:

0th order

$$[\mathbf{v} \cdot \nabla_r - (1/m) \nabla_r U \cdot \nabla_v] F_0 = 0, \quad (12)$$

1st order

$$[\mathbf{v} \cdot \nabla_r - (1/m) \nabla_r U \cdot \nabla_v] F_1 = (i/2m) [\nabla_r^2 F_0 - (1/m) (\nabla_r \cdot \nabla_r)^2 U F_0], \quad (13)$$

2nd order

$$\begin{aligned} & \left( \mathbf{v} \cdot \nabla_r - \frac{1}{m} \nabla_r U \cdot \nabla_v \right) F_2 \\ &= -\frac{i}{2m} \left[ \nabla_r^2 F_1 - \frac{1}{m} (\nabla_r \cdot \nabla_r)^2 U F_1 \right] - \frac{1}{6m^3} (\nabla_r \cdot \nabla_r)^3 U F_0 \\ &+ \frac{2\pi e^2 N-1}{m^3 N} [\nabla_r g_0 \cdot \nabla_r F_0 - \nabla_r F_0 \cdot \nabla_r g_0], \end{aligned} \quad (14)$$

where

$$g_0(\mathbf{r}, \mathbf{v}) = \int \frac{d^3v'}{|\mathbf{v} - \mathbf{v}'|^2} F_0(\mathbf{r}, \mathbf{v}'), \quad (15)$$

etc. The potential energy  $U$  is then rendered self-consistent by introducing into (2) and (3) the quantity  $\bar{F}(U; \mathbf{r}, \mathbf{v})$ . (We indicate here explicit dependence of  $\bar{F}$  on  $U$ .)

Generally, the series (10) will only be partially summed. Defining the  $p$ th approximation to  $\bar{F}$

$$\bar{F}^{(p)}(U; \mathbf{r}, \mathbf{v}) = \sum_{n=0}^p \hbar^n F_n(U; \mathbf{r}, \mathbf{v}), \quad (16)$$

the corresponding approximation  $U^{(p)}$  to the potential is then determined from

$$\nabla^2 U^{(p)} = -4\pi e^2 \frac{N-1}{N} \int d^3v \bar{F}^{(p)}(U^{(p)}; \mathbf{r}, \mathbf{v}), \quad (17)$$

$$\lim_{r \rightarrow 0} U^{(p)} = -\frac{Ze^2}{r}, \quad U^{(p)} \sim_{r \rightarrow \infty} \frac{(Z-N+1)e^2}{r}, \quad (18)$$

a procedure which guarantees the self-consistency of the potential at every stage of approximation.

### Solution to Second Order

In this paper, we shall consider only corrections to order  $\hbar^2$  and hence will require  $\tilde{F}^{(2)}$ . Before proceeding to the consideration of special cases, it is useful to point certain simplifications of the relevant equations [(12)–(14)] which can be made in general. First, making use of (12), it is not difficult to show that (13) can be immediately solved to yield

$$F_1 = (-i/2m)\nabla_{\mathbf{r}}^2 F_0, \quad (19)$$

where

$$\nabla_{\mathbf{r}}^2 F_0 = \partial^2 F_0 / \partial x_i \partial x_i. \quad (20)$$

Second, again making use of (12), one can establish the identity

$$(\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{v}})^4 U F_0 = 2m[\nabla_{\mathbf{r}}^2 (\nabla_{\mathbf{r}}^2 F_0) - (1/m)(\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{v}})^2 U \nabla_{\mathbf{r}}^2 F_0] + m[\mathbf{v} \cdot \nabla_{\mathbf{r}} (\nabla_{\mathbf{r}}^4 F_0) - (1/m)\nabla_{\mathbf{r}} U \cdot \nabla_{\mathbf{v}} (\nabla_{\mathbf{r}}^4 F_0)], \quad (21)$$

where

$$\nabla_{\mathbf{r}}^4 F_0 = \partial^4 F_0 / \partial x_i \partial x_j \partial x_k \partial x_l. \quad (22)$$

Introducing (19) and (21) into (14), there follows

$$F_2 = -(1/8m^2)\nabla_{\mathbf{r}}^4 F_0 + G_2, \quad (23)$$

where

$$\left(\mathbf{v} \cdot \nabla_{\mathbf{r}} - \frac{1}{m}\nabla_{\mathbf{r}} U \cdot \nabla_{\mathbf{v}}\right) G_2 = -\frac{1}{24m^3}(\nabla_{\mathbf{r}} \cdot \nabla_{\mathbf{v}})^3 U F_0 + \frac{2\pi e^2 N - 1}{m^3 N} [\nabla_{\mathbf{r}} g_0 \cdot \nabla_{\mathbf{r}} F_0 - \nabla_{\mathbf{r}} F_0 \cdot \nabla_{\mathbf{r}} g_0]. \quad (24)$$

Thus, all that remains is to determine  $F_0$ . Since we are concerned here with the ground state of the system, the  $F_0$  we seek is that solution of the Vlasov equation (12) corresponding to minimum total energy and maximum entropy.

### III. ATOM OR ION WITH NONZERO ORBITAL ANGULAR MOMENTUM

As is well known, the most general solution to the Vlasov equation is any functional of the constants of the motion of a particle moving in the potential  $U(\mathbf{r})$ . We consider an atom or ion with total orbital angular momentum  $J\mathbf{L}$ , where  $\mathbf{L}$  is a unit vector. It is clear that the potential in this case has rotational symmetry about  $\mathbf{L}$ , i.e.,

$$\nabla_{\mathbf{r}} U \cdot \mathbf{r} \times \mathbf{L} = 0. \quad (25)$$

A particle moving in such a potential has only two constants of the motion: the total energy  $\frac{1}{2}mv^2 + U(\mathbf{r})$  and the projection of the orbital angular momentum along  $\mathbf{L}$ , i.e.,  $m\mathbf{r} \times \mathbf{v} \cdot \mathbf{L}$ . Thus, the most general solution to the Vlasov equation in this case is any functional of the form

$$F_0 = F_0(\frac{1}{2}mv^2 + U(\mathbf{r}), m\mathbf{r} \times \mathbf{v} \cdot \mathbf{L}). \quad (26)$$

To minimize the total energy,  $\int \int [\frac{1}{2}mv^2 + U(\mathbf{r})] \times F_0(\mathbf{r}, \mathbf{v}) d^3\mathbf{r} d^3\mathbf{v}$ , we clearly seek that distribution in velocity space which locally minimizes  $(m/2) \int v^2 F_0(\mathbf{r}, \mathbf{v}) \times d^3\mathbf{v}$  subject to the constraints of fixed spatial density  $\int F_0 d^3\mathbf{v}$  and fixed local momentum density  $\int m\mathbf{v} F_0 d^3\mathbf{v}$ . It is easily shown that this requirement is met if  $F_0$  possesses spherical symmetry in velocity space (about some displaced origin), i.e.,

$$F_0 = F_0([\mathbf{v} - \mathbf{d}(\mathbf{r})]^2, e(\mathbf{r})), \quad (27)$$

where  $\mathbf{d}$  and  $e$  are arbitrary functions of  $\mathbf{r}$ . Combining (26) and (27) leads to a unique form of the minimum energy solution to the Vlasov equation

$$F_0 = F_0(U(\mathbf{r}) + \frac{1}{2}mv^2 - m\omega\mathbf{r} \times \mathbf{v} \cdot \mathbf{L}), \quad (28)$$

where  $\omega$  is a constant. Note that this implies uniform rotation with angular frequency  $\omega$ . If we transform to the rotating frame, the transformed density function  $F_0'$  is

$$F_0' = F_0'(U(\mathbf{r}') + \frac{1}{2}mv'^2 - \frac{1}{2}m\omega^2(\mathbf{r}' \times \mathbf{L})^2), \quad (29)$$

and is therefore a function solely of the energy  $\epsilon'$ , in the rotating frame, where the effective potential energy is

$$U_{\text{eff}} = U(\mathbf{r}') - \frac{1}{2}m\omega^2(\mathbf{r}' \times \mathbf{L})^2. \quad (30)$$

The entropy maximization in the rotating frame yields, of course, the Fermi distribution, i.e.,

$$F_0'(\epsilon') = F_0(\epsilon') = 2\left(\frac{m}{h}\right)^3 \left[ \exp\left(\frac{\epsilon' - \lambda}{kT}\right) + 1 \right]^{-1}. \quad (31)$$

The function  $F_0$  is therefore determined, and we have finally

$$F_0 = 2\left(\frac{m}{h}\right)^3 \times \left[ \exp\left(\frac{U(\mathbf{r}) + \frac{1}{2}mv^2 - m\omega\mathbf{r} \times \mathbf{v} \cdot \mathbf{L} - \lambda}{kT}\right) + 1 \right]^{-1}. \quad (32)$$

The Thomas-Fermi (Amaldi) model, generalized to nonzero angular momentum and nonzero temperature, follows from (32), (17), and (18) if  $p=0$ , i.e., if we use only the lowest order approximation to  $\tilde{F}$ . In the limit of zero temperature, this leads to the equations first derived and studied by Sessler and Foley.<sup>6</sup> For zero angular momentum, we obtain the usual finite-temperature Thomas-Fermi model.<sup>5</sup>

### IV. QUANTUM AND EXCHANGE CORRECTIONS

Using the  $F_0$  given by (32), we shall now go to second order in  $\hbar$  and compute  $\tilde{F}^{(2)}$ . From (19), (25), and (32)



there follows immediately

$$F_1 = (-i/2)[\mathbf{v} \cdot \nabla_r U + m\omega^2 \mathbf{v} \times \mathbf{L} \cdot \mathbf{L} \times \mathbf{r}] F_0'', \quad (33)$$

where the primes indicate differentiation of  $F_0$  with respect to its argument, i.e.,

$$F_0' = \left\{ \frac{d}{dx} 2 \left( \frac{m}{h} \right)^3 \times \left[ \exp \left( \frac{x-\lambda}{kT} \right) + 1 \right]^{-1} \right\}_{x = U^{(2)} + \frac{1}{2} m \omega^2 - m \omega \mathbf{r} \times \mathbf{v} \cdot \mathbf{L}} \quad (34)$$

The solution of (23) and (24) for  $F_2$ , while simple and straightforward in the absence of angular momentum, is somewhat involved in the general case and is therefore delegated to the Appendix. The result is

$$F_2 = -\frac{1}{4m} F_0'' \nabla_r^2 U - \frac{1}{6} F_0''' \left[ \mathbf{v} \cdot \nabla_r (\mathbf{v} \cdot \nabla_r U) + \frac{1}{m} \nabla_r U \cdot \nabla_r U \right] + \frac{\omega}{2} F_0''' \mathbf{v} \cdot \mathbf{L} \times \nabla_r U - \frac{1}{6} F_0'''' \times \{ \mathbf{v} \cdot \nabla_r [U - \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2] \}^2 - \frac{2\pi e^2 N - 1}{m^2 N} F_0' \times \int \frac{d^3 v'}{|\mathbf{v} - \mathbf{v}'|^2} F_0(\mathbf{r}, \mathbf{v}'). \quad (35)$$

Introducing (32), (34), and (35) into (17) and (18) and performing the angular integrations in velocity space [keeping in mind the symmetry condition (25)] leads after some algebra to the following equation for  $U^{(2)}$ :

$$\nabla^2 U^{(2)} = -\frac{4e^2 (2m)^{\frac{1}{2}} N - 1}{3\hbar^3} \left\{ \frac{3}{2} \int_0^\infty d\omega \omega^{-\frac{1}{2}} f_0(\omega + U^{(2)} - \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2) + \frac{\hbar^2}{16m} \nabla^2 U^{(2)} \int_0^\infty d\omega \omega^{-\frac{1}{2}} f_0'(\omega + U^{(2)} - \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2) + \frac{\hbar^2}{32} \frac{1}{m} \nabla U^{(2)} \cdot \nabla U^{(2)} - \omega^2 \nabla U^{(2)} \cdot \nabla (\mathbf{L} \times \mathbf{r})^2 - \frac{3}{4} m \omega^4 [\nabla (\mathbf{L} \times \mathbf{r})^2]^2 \right\} \int_0^\infty d\omega \omega^{-\frac{1}{2}} f_0''(\omega + U^{(2)} - \frac{1}{2} m \omega^2 (\mathbf{v} \times \mathbf{L})^2) + \frac{3e^2 (2m)^{\frac{1}{2}} N - 1}{8\pi\hbar} \left[ \int_0^\infty d\omega \omega^{-\frac{1}{2}} f_0(\omega + U^{(2)} - \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2) \right]^2, \quad (36)$$

where

$$f_0(x) = \left[ \exp \left( \frac{x-\lambda}{kT} \right) + 1 \right]^{-1}, \quad (37)$$

and  $U^{(2)}$  satisfies the boundary conditions

$$U^{(2)} \sim -(Z - N + 1)e^2/r, \quad (38)$$

$$\lim_{r \rightarrow 0} U^{(2)} = -Ze^2/r. \quad (39)$$

In the limit of zero temperature, the integrals occurring in (36) can be easily performed, yielding

$$\nabla^2 U^{(2)} = -\frac{4e^2}{3\pi\hbar^3} \frac{N-1}{N} \left\{ 2m[\lambda - U^{(2)} + \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2] \right\}^{\frac{1}{2}} \left\{ 1 - \frac{\hbar^2}{16m} \nabla^2 U^{(2)} [\lambda - U^{(2)} + \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2]^{-\frac{1}{2}} - \frac{\hbar^2}{64} [\lambda - U^{(2)} + \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2]^{-\frac{3}{2}} \left[ \frac{1}{m} \nabla U^{(2)} \cdot \nabla U^{(2)} - \omega^2 \nabla U^{(2)} \cdot \nabla (\mathbf{L} \times \mathbf{r})^2 - \frac{3}{4} m \omega^4 [\nabla (\mathbf{L} \times \mathbf{r})^2]^2 \right] + \frac{3e^2 (2m)^{\frac{1}{2}} N - 1}{2\pi\hbar} \frac{N-1}{N} [\lambda - U^{(2)} + \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2]^{-\frac{1}{2}} \right\}. \quad (40)$$

To establish contact with previously published results,<sup>4</sup> we pass to the limit of zero angular momentum ( $\omega \rightarrow 0$ ) in (40) and let

$$U^{(2)} = U_0 + \hbar^2 U_2, \quad (41)$$

where  $U_0$  is the solution of the usual Thomas-Fermi (Amaldi) equation:

$$\nabla^2 U_0 = -\frac{4e^2}{3\pi\hbar^3} \frac{N-1}{N} [2m(\lambda - U_0)]^{\frac{1}{2}}. \quad (42)$$

Assuming  $\hbar^2 U_2 \ll U_0$  so that only the lowest order terms are kept, (40) becomes

$$-\nabla^2 U_2 + \frac{4me^2}{\pi\hbar^3} \frac{N-1}{N} [2m(\lambda - U_0)]^{\frac{1}{2}} U_2 = \frac{8m^2 e^4}{\pi^2 \hbar^6} \left( \frac{N-1}{N} \right)^2 (\lambda - U_0) - \frac{me^2}{12\pi\hbar^3} \frac{N-1}{N} [2m(\lambda - U_0)]^{-\frac{1}{2}} \times [4\nabla^2 U_0 + (\lambda - U_0)^{-1} \nabla U_0 \cdot \nabla U_0], \quad (43)$$

which is the usual quantum and exchange correction to the Thomas-Fermi model,<sup>15</sup> augmented by the Fermi-Amaldi  $(N-1)/N$  factor. Note that the perturbation procedure used to obtain (43) from (40) destroys the self-consistency of the potential.

Equations (36) and (37) contain two constants which require some discussion. The chemical potential  $\lambda$  is essentially determined by the boundary condition (38). The determination of the angular frequency  $\omega$  depends on the problem being studied. That is, if the total angular momentum  $\mathbf{J}$  is put in as an *ad hoc* constraint, then<sup>16</sup>  $\omega$  is determined from

$$\mathbf{J} = \int \int d^3r d^3v m \mathbf{r} \times \mathbf{v} \tilde{F}^{(2)}(\mathbf{r}, \mathbf{v}). \quad (44)$$

On the other hand, in the spirit of the statistical approach to the atom, one may determine  $\omega$  from the model itself, as that which minimizes the total energy. This point will be explored more fully elsewhere.

### V. CORRELATIONS

The "quantum plasma" approach to the statistical atom presented here, establishes a connection between contemporary problems in plasma physics and the difficult problem of introducing correlations into the Thomas-Fermi model. Correlations are introduced in classical plasma physics by higher order truncations of the BBGKY hierarchy. Thus, for example, instead of decomposing the doublet distribution function into a product of singlet functions, the *triplet* distribution function is decomposed into products of singlet and doublet functions. This results in a complicated set of coupled equations for the singlet and doublet distributions.<sup>9</sup> A precisely analogous procedure can be carried through for the q.m.d.f. An expansion of the singlet and doublet q.m.d.f. in powers of  $\hbar$  can then be performed, leading to essentially the classical equations in lowest order. Recalling that the Thomas-Fermi "approach" is wholly tantamount to the solution of these lowest order equations, it is clear that *to introduce correlations into the Thomas-Fermi model, one must begin by finding the classical doublet distribution function for a spatially inhomogeneous plasma whose singlet function is the Fermi distribution.* This problem is as yet unsolved.

### APPENDIX. SOLUTION FOR $F_2$

We present here the solution of (23) and (24), where

$$F_0 = F_0(U(\mathbf{r}) + \frac{1}{2}m\mathbf{v}^2 - m\omega\mathbf{v} \cdot \mathbf{L} \times \mathbf{r}). \quad (A1)$$

Let

$$F_2 = F_2^A + F_2^B + F_2^C, \quad (A2)$$

where

$$F_2^A = -\frac{1}{8m^2} \nabla_r^2 F_0 \quad (A3)$$

$$\left( \mathbf{v} \cdot \nabla_r - \frac{1}{m} \nabla_r U \cdot \nabla_v \right) F_2^B = -\frac{1}{24m^3} (\nabla_r \cdot \nabla_v)^2 U F_0, \quad (A4)$$

and

$$\left( \mathbf{v} \cdot \nabla_r - \frac{1}{m} \nabla_r U \cdot \nabla_v \right) F_2^C = \frac{2\pi e^2 N - 1}{m^3 N} (\nabla_v g_0 \cdot \nabla_r F_0 - \nabla_v F_0 \cdot \nabla_r g_0). \quad (A5)$$

In solving these equations, use is continually made of the symmetry condition (25) and related identities like:

$$\mathbf{v} \cdot \nabla_r (\mathbf{L} \times \mathbf{r} \cdot \nabla_r U) = \mathbf{L} \times \mathbf{r} \cdot \nabla_r (\mathbf{L} \times \mathbf{r} \cdot \nabla_r U) = 0, \quad (A6)$$

etc., to reduce the complexity of the multiple vector and tensor products which formally arise. As space does not permit these manipulations to be exhibited in detail, we present only the skeleton of the calculation.

(A-3) involves only the straightforward evaluation of  $\nabla_r^2 F_0$ , and we find

$$\begin{aligned} F_2^A = & -(1/8m) F_0'' \nabla^2 U - \frac{1}{8} F_0''' [\mathbf{v} \cdot \nabla_r (\mathbf{v} \cdot \nabla U) \\ & + (1/m) (\nabla U)^2] + \frac{1}{4} \omega F_0''' \mathbf{v} \cdot \mathbf{L} \times \nabla U \\ & + \frac{1}{16} \omega^2 F_0''' \nabla_r (\mathbf{L} \times \mathbf{r})^2 \cdot \nabla U + \frac{1}{8} m \omega^2 F_0''' \\ & \times (\mathbf{v} \times \mathbf{L})^2 - F_0''' \{ \mathbf{v} \cdot \nabla_r [U - \frac{1}{2} m \omega^2 (\mathbf{L} \times \mathbf{r})^2] \}^2 \\ & + \{ \frac{1}{2} m \omega^2 (F_0'' - \omega F_0''') \mathbf{v} \cdot \mathbf{L} \times \mathbf{r} \}. \end{aligned} \quad (A7)$$

The last term in curly brackets being a solution of the homogeneous (Vlasov) equation is then deleted since we are only interested in the (inhomogeneous) terms generated directly by the right hand side of (14). Its appearance in (A7) is a formal consequence of the shortcut (21), and care must consequently be taken when evaluating (A3) to delete these spurious terms.

The only real algebraic complexity arises in (A4). Straightforward evaluation of the right-hand side yields.

$$\begin{aligned} & -\frac{1}{24m^3} (\nabla_r \cdot \nabla_v)^2 U F_0 \\ & = -\frac{1}{8m} \{ [\mathbf{v} - \omega (\mathbf{L} \times \mathbf{r})] \cdot \nabla_r [\nabla_r^2 U] \} F_0'' \\ & \quad - \frac{1}{24} (\mathbf{v} - \omega \mathbf{L} \times \mathbf{r})_i (\mathbf{v} - \omega \mathbf{L} \times \mathbf{r})_j (\mathbf{v} - \omega \mathbf{L} \times \mathbf{r})_k \\ & \quad \times \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k} F_0'''. \end{aligned} \quad (A8)$$

It is not difficult to show that as a consequence of (25),

$$\begin{aligned} & \mathbf{L} \times \mathbf{r} \cdot \nabla_r (\nabla_r^2 U) \\ & = 0 = (\mathbf{L} \times \mathbf{r})_i (\mathbf{L} \times \mathbf{r})_j (\mathbf{L} \times \mathbf{r})_k \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k}. \end{aligned} \quad (A9)$$

<sup>15</sup> See, for example, Eq. (4.15) of reference 7.

<sup>16</sup> More properly  $\omega^{(2)}$ , in the sense of the definition (16).

Consequently, (A8) becomes

$$\begin{aligned} & -\frac{1}{24m^2}(\nabla_r \cdot \nabla_r)^2 U F_0' \\ & = -\frac{1}{8m}[\mathbf{v} \cdot \nabla(\nabla^2 U)]F_0'' - \frac{1}{24}[\mathbf{v} \cdot \nabla_r(\mathbf{v} \cdot \nabla_r(\mathbf{v} \cdot \nabla U))]F_0''' \\ & \quad + \frac{1}{8}\omega(\mathbf{L} \times \mathbf{r})_{,j}v_{j,k} \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k} F_0''' - \frac{1}{8}\omega^2(\mathbf{L} \times \mathbf{r})_{,i}(\mathbf{L} \times \mathbf{r})_{,j}v_{j,k} \\ & \quad \times \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k} F_0''. \quad (\text{A10}) \end{aligned}$$

The contribution of the first two terms of (A10) to  $F_2^B$  is immediately found, since it is readily verified that

$$\begin{aligned} & \left( \mathbf{v} \cdot \nabla_r - \frac{1}{m} \nabla_r U \cdot \nabla_r \right) \left( -\frac{1}{8m} F_0'' \nabla^2 U - \frac{1}{24} F_0''' \right. \\ & \quad \times \left[ \mathbf{v} \cdot \nabla_r(\mathbf{v} \cdot \nabla U) + \frac{1}{m} (\nabla U)^2 \right] \Big) \\ & = -\frac{1}{8m}[\mathbf{v} \cdot \nabla(\nabla^2 U)]F_0'' - \frac{1}{24} \\ & \quad \times \mathbf{v} \cdot \nabla_r[\mathbf{v} \cdot \nabla_r(\mathbf{v} \cdot \nabla U)]F_0'''. \quad (\text{A11}) \end{aligned}$$

The contribution arising from the remaining terms of (A10) proceeds as follows. Using the identity

$$\mathbf{v} \cdot \nabla_r[\mathbf{v} \cdot \nabla_r(\mathbf{L} \times \mathbf{v} \cdot \nabla U)] = 0, \quad (\text{A12})$$

one finds

$$\begin{aligned} & \frac{1}{8}\omega(\mathbf{L} \times \mathbf{r})_{,j}v_{j,k} \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k} F_0''' \\ & = \frac{1}{8}\omega \mathbf{v} \times \mathbf{L} \cdot \nabla_r(\mathbf{v} \cdot \nabla U) F_0'''. \quad (\text{A13}) \end{aligned}$$

This leads to a contribution to  $F_2^B$  of

$$\frac{1}{8}\omega F_0''' \mathbf{v} \times \mathbf{L} \cdot \nabla U, \quad (\text{A14})$$

which can be verified by direct substitution into the left-hand side of (A4).

In a similar fashion, use of the identity

$$\mathbf{L} \times \mathbf{r} \cdot \nabla_r(\mathbf{v} \cdot \nabla_r(\mathbf{L} \times \mathbf{r} \cdot \nabla U)) = 0. \quad (\text{A15})$$

leads, after some algebra, to the relation

$$\begin{aligned} & (\mathbf{L} \times \mathbf{r})_{,i}(\mathbf{L} \times \mathbf{r})_{,j}v_{j,k} \frac{\partial^3 U}{\partial x_i \partial x_j \partial x_k} \\ & = \frac{1}{2} \mathbf{v} \cdot \nabla_r[\nabla_r(\mathbf{L} \times \mathbf{r})^2 \cdot \nabla U] - \nabla_r(\mathbf{L} \times \mathbf{v})^2 \cdot \nabla_r U. \quad (\text{A16}) \end{aligned}$$

The contribution to  $F_2^B$  arising from the last term of (A10) is immediately apparent and is

$$-\frac{1}{8}\omega^2 F_0''' [\nabla_r(\mathbf{L} \times \mathbf{r})^2 \cdot \nabla U + 2m(\mathbf{L} \times \mathbf{v})^2]. \quad (\text{A17})$$

Collecting terms, there follows for  $F_2^B$ :

$$\begin{aligned} F_2^B = & -\frac{1}{8m} F_0'' \nabla^2 U - \frac{1}{24} F_0''' \left[ \mathbf{v} \cdot \nabla_r(\mathbf{v} \cdot \nabla U) + \frac{1}{m} (\nabla U)^2 \right] \\ & + \frac{1}{8}\omega F_0''' \mathbf{v} \times \mathbf{L} \cdot \nabla U - \frac{1}{8}m\omega^2 F_0''' (\mathbf{L} \times \mathbf{v})^2 \\ & - \frac{1}{8}\omega^2 F_0''' \nabla(\mathbf{L} \times \mathbf{r})^2 \cdot \nabla U. \quad (\text{A18}) \end{aligned}$$

Finally  $F_2^C$ , the contribution arising from exchange, is readily obtained since the right-hand side of (A5) becomes

$$\begin{aligned} & -\frac{2\pi e^2 N-1}{m^2 N} \left[ \mathbf{v} \cdot \nabla_r g_0 - \frac{1}{m} \nabla_r U \cdot \nabla_r g_0 \right] F_0' \\ & + \frac{2\pi e^2 N-1}{m^2 N} \omega [\mathbf{L} \times \mathbf{r} \cdot \nabla_r g_0 - \mathbf{v} \times \mathbf{L} \cdot \nabla_r g_0] F_0'. \quad (\text{A19}) \end{aligned}$$

It is not difficult to show that the second term of (A19) vanishes identically. Consequently, we have immediately

$$F_2^C = -\frac{2\pi e^2 N-1}{m^2 N} g_0 F_0'. \quad (\text{A20})$$



## Appendix B.

Derivation of Exchange-Corrected Energy Transport Equation

This Appendix is devoted to the derivation of equation IV-118. The starting point is equation III-48 with the additional exchange term IV-117. Specifically,

$$\begin{aligned} & \frac{\partial}{\partial t} \left[ \int d^3v \frac{1}{2} m v^2 \tilde{F}^{(1)} \right] + \nabla \cdot \left[ \int d^3v \underline{v} \frac{1}{2} m v^2 \tilde{F}^{(1)} - \frac{i\hbar}{2m} \nabla \int d^3v \frac{1}{2} m v^2 \tilde{F}^{(1)} \right] \\ & + g^2 \nabla \phi_T \cdot \left[ \int d^3v \underline{v} \tilde{F}^{(1)} \right] + \frac{i g^2 \hbar}{2m} \nabla^2 \phi_T \left[ \int d^3v \tilde{F}^{(1)} \right] \\ & - g^2 \int d^3v \frac{v^2}{2} \left( \frac{\partial \phi^{exch}}{\partial x^k} \frac{\partial \tilde{F}^{(1)}}{\partial v^k} - \frac{\partial \phi^{exch}}{\partial v^k} \frac{\partial \tilde{F}^{(1)}}{\partial x^k} \right) = 0 \end{aligned} \quad (B-1)$$

Denoting the last term temporarily by  $\{exch\}$ , we introduce the ansatz III-66 and take the real part of B-1 to obtain

$$\begin{aligned} & \frac{\partial}{\partial t} \left[ \text{Re} \int d^3w \frac{1}{2} m (\underline{w} + \langle \underline{u} \rangle)^2 \tilde{F}^{(1)'}(\underline{x}, \underline{w}, t) \right] + \nabla \cdot \left[ \text{Re} \int d^3w (\underline{w} + \langle \underline{u} \rangle) \frac{1}{2} m (\underline{w} + \langle \underline{u} \rangle)^2 \tilde{F}^{(1)'}(\underline{x}, \underline{w}, t) \right. \\ & \left. + \frac{\hbar}{2m} \nabla \int d^3v \frac{1}{2} m v^2 \tilde{F}^{(1)}(\underline{x}, \underline{v}, t) \right] + g^2 \nabla \phi_T \cdot \text{Re} \int d^3w (\underline{w} + \langle \underline{u} \rangle) \tilde{F}^{(1)'}(\underline{x}, \underline{w}, t) \\ & + \text{Re} \{exch\} = 0 \end{aligned} \quad (B-2)$$

Next, making use of III-69, III-72 and III-73, as well as III-49, converts this equation into

$$\begin{aligned} & \frac{\partial}{\partial t} \left[ \frac{1}{2} m \langle \underline{u} \rangle^2 \langle n \rangle + \frac{1}{2} \text{Tr} \langle \Pi' \rangle \right] + \frac{\partial}{\partial x^k} \left\{ \langle u^k \rangle \langle \Pi'^{kl} \rangle + \langle u^k \rangle \frac{1}{2} \text{Tr} \langle \Pi' \rangle \right. \\ & \left. + \langle u^k \rangle \frac{1}{2} m \langle n \rangle \langle \underline{u} \rangle^2 + \frac{\hbar^2}{4m} \frac{\partial}{\partial x^k} \left( \nabla \cdot (\langle n \rangle \langle \underline{u} \rangle) \right) + \text{Re} \int d^3w w^k \frac{1}{2} m w^2 \tilde{F}^{(1)'}(\underline{x}, \underline{w}, t) \right\} \\ & + g^2 (\nabla \phi_T \cdot \langle \underline{u} \rangle) \langle n \rangle + \text{Re} \{exch\} = 0 \end{aligned} \quad (B-3)$$

Introducing the definitions III-77 and III-78 and employing the mass continuity equation (III-56) yields

$$\begin{aligned} m\langle n \rangle \left( \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right) \langle \bar{\epsilon}' \rangle^{kin} + \langle \pi' \rangle \cdot \underline{\nabla} \langle \underline{u} \rangle + \underline{\nabla} \cdot \langle \underline{Q}' \rangle \\ - \frac{\partial}{\partial t} \left( \frac{\hbar^2}{4m} \nabla^2 \langle n \rangle \right) + \frac{\partial}{\partial t} \left( \frac{m}{2} \langle n \rangle \langle \underline{u} \rangle^2 \right) + \underline{\nabla} \cdot \left( \underline{u} \frac{1}{2} m \langle n \rangle \langle \underline{u} \rangle^2 \right) \\ + \langle u^L \rangle \frac{\partial}{\partial x^k} \langle \pi'^{KL} \rangle + g^2 \langle n \rangle \langle \underline{u} \rangle \cdot \underline{\nabla} \phi_T + Re \{exch\} = 0 \end{aligned}$$

(B-4)

Finally, noting that since by virtue of III-56

$$\frac{\partial}{\partial t} \left( \frac{m}{2} \langle n \rangle \langle \underline{u} \rangle^2 \right) + \underline{\nabla} \cdot \left( \langle \underline{u} \rangle \frac{1}{2} m \langle n \rangle \langle \underline{u} \rangle^2 \right) = m \langle n \rangle \langle \underline{u} \rangle \cdot \left( \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right) \langle \underline{u} \rangle$$

(B-5)

we can replace these two terms by the scalar product of  $\langle \underline{u} \rangle$  and the momentum conservation equation (IV-107). The end result of this operation is the equation

$$\begin{aligned} m\langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \langle \bar{\epsilon}' \rangle^{kin} + \langle \pi' \rangle \cdot \underline{\nabla} \langle \underline{u} \rangle + \underline{\nabla} \cdot \langle \underline{Q}' \rangle \\ - \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \left( \frac{\hbar^2}{4m} \nabla^2 \langle n \rangle \right) - \langle \underline{u} \rangle \cdot \underline{\nabla} \langle \rho'^{exch} \rangle + Re \{exch\} = 0 \end{aligned}$$

(B-6)

which can also be written as

$$\begin{aligned} m\langle n \rangle \left[ \frac{\partial}{\partial t} + \langle \underline{u} \rangle \cdot \underline{\nabla} \right] \left( \langle \bar{\epsilon}' \rangle^{kin} - \frac{\hbar^2}{4m^2} \frac{\nabla^2 \langle n \rangle}{\langle n \rangle} \right) + \langle \pi' \rangle \cdot \underline{\nabla} \langle \underline{u} \rangle \\ + \frac{\hbar^2}{4m} (\nabla^2 \langle n \rangle) \underline{\nabla} \cdot \langle \underline{u} \rangle + \underline{\nabla} \cdot \langle \underline{Q}' \rangle - \langle \underline{u} \rangle \cdot \underline{\nabla} \langle \rho' \rangle^{exch} + Re \{exch\} = 0 \end{aligned}$$

(B-7)

In the absence of exchange, this is equation III-76.

Turning finally to  $\text{Re} \{ \text{exch} \}$ , we first integrate by parts to obtain

$$\begin{aligned} \text{Re} \{ \text{exch} \} &\equiv \text{Re} \left[ -g^2 \int d^3v \frac{1}{2} v^2 \left( \frac{\partial \phi^{\text{exch}}}{\partial x^k} \frac{\partial \tilde{F}^{(1)}}{\partial v^k} - \frac{\partial \phi^{\text{exch}}}{\partial v^k} \frac{\partial \tilde{F}^{(1)}}{\partial x^k} \right) \right] \\ &= \text{Re} \left[ -g^2 \frac{\partial}{\partial x^k} \int d^3v \frac{1}{2} v^2 \phi^{\text{exch}} \frac{\partial \tilde{F}^{(1)}}{\partial v^k} - g^2 \int d^3v v^k \phi^{\text{exch}} \frac{\partial \tilde{F}^{(1)}}{\partial x^k} \right] \quad (\text{B-8}) \end{aligned}$$

Next, introduction of the ansatz IV-104 together with the fact that  $F_0(\underline{x}, \underline{w}, t)$  (as defined in IV-105) and, consequently,  $\phi_0^{\text{exch}}(\underline{x}, \underline{w}, t)$  depend only on the magnitude of  $\underline{w}$  lead to

$$\begin{aligned} \text{Re} \{ \text{exch} \} &= -g^2 \frac{\partial}{\partial x^k} \int d^3w \frac{1}{2} (\underline{w} + \langle \underline{u} \rangle)^2 \phi_0^{\text{exch}}(\underline{x}, \underline{w}, t) \frac{\partial F_0(\underline{x}, \underline{w}, t)}{\partial (\frac{1}{2} m w^2)} m w^k \\ &\quad - g^2 \int d^3w (\underline{w} + \langle \underline{u} \rangle)^k \phi_0^{\text{exch}}(\underline{x}, \underline{w}, t) \frac{\partial F_0(\underline{x}, \underline{w}, t)}{\partial x^k} \quad (\text{B-9}) \\ &= -g^2 \frac{\partial}{\partial x^k} \left[ \langle u^k \rangle \int d^3w \frac{m w^2}{3} \phi_0^{\text{exch}}(\underline{x}, \underline{w}, t) \frac{\partial F_0}{\partial (\frac{1}{2} m w^2)} \right] - g^2 \langle u^k \rangle \int d^3w \phi_0^{\text{exch}}(\underline{x}, \underline{w}, t) \frac{\partial F_0(\underline{x}, \underline{w}, t)}{\partial x^k} \end{aligned}$$

Inserting the definition (IV-100) of the exchange potential, we arrive at

$$\begin{aligned} \text{Re} \{ \text{exch} \} &= \underline{\nabla} \cdot \left[ \langle \underline{u} \rangle \int d^3w \frac{m w^2}{6} \frac{\partial F_0}{\partial (\frac{1}{2} m w^2)} \left( g^2 \int d^3w' f\left(\frac{m}{\hbar}(\underline{w}' - \underline{w})\right) F_0(\underline{x}, \underline{w}', t) \right) \right] \\ &\quad + \langle \underline{u} \rangle \cdot \underline{\nabla} \int d^3w \frac{F_0(\underline{x}, \underline{w}, t)}{4} \left( g^2 \int d^3w' f\left(\frac{m}{\hbar}(\underline{w}' - \underline{w})\right) F_0(\underline{x}, \underline{w}', t) \right) \quad (\text{B-10}) \end{aligned}$$

Making use of IV-108 and IV-119, we obtain finally

$$\text{Re} \{ \text{exch} \} = \langle \underline{u} \rangle \cdot \underline{\nabla} \langle p' \rangle^{\text{exch}} + \left( \langle p' \rangle^{\text{exch}} + \langle \epsilon' \rangle^{\text{exch}} \right) \underline{\nabla} \cdot \langle \underline{u} \rangle \quad (\text{B-11})$$

which, when inserted into B-7, yields IV-118.



Appendix C

Solution of Time-Independent Quantum Vlasov Equation to Order  $\hbar^2$

We consider in this Appendix the method for obtaining a solution of the equation

$$\left\{ F(r, v), H(r, v) \right\}_{G.P.B.}^{(1)} = 0 \quad (C-1)$$

of the form

$$F(r, v) = \sum_{n=0}^{\infty} F_n(r, v) \hbar^n \quad (C-2)$$

where  $H$  is an arbitrary single-particle Hamiltonian. Both the first and second time-independent quantum Vlasov equations are thus included in this category. We ignore for the moment the fact that  $H$  itself may depend on  $\hbar$  either explicitly or implicitly via a dependence on  $F$ , and consider it to be some given function.

Introducing the convenient notation

$$\frac{\partial^{(m+n)} A}{(\partial x_i \partial x_j \dots)(\partial v_k \partial v_l \dots)} \equiv A_{ij \dots}^{kl \dots} \quad (C-3)$$

$\uparrow$   
 $m$  space derivatives

where  $i, j, k, l, \dots$  are Cartesian indices, and the operator  $\uparrow$ :

$$\uparrow A_{ij \dots}^{kl \dots} \equiv A_{kl \dots}^{ij \dots} \quad (C-4)$$

we find from the definition of the G.P.B (II-57 and II-53) that  $F_0$ ,  $F_1$ , and  $F_2$  satisfy the equations

$$\frac{1}{m} \left\{ F_0, H \right\}_{P.B.}^{(1)} \equiv \frac{1}{m} (1 - \uparrow) F_0; H^j = 0 \quad (C-5)$$

$$\frac{1}{m} (1 - \updownarrow) F_{,j} H^j = \frac{i}{2m^2} (1 - \updownarrow) F_{,j k} H^{j k} \quad (C-6)$$

$$\frac{1}{m} (1 - \updownarrow) F_{,j} H^j = \frac{i}{2m^2} (1 - \updownarrow) F_{,j k} H^{j k} + \frac{1}{6m^3} (1 - \updownarrow) F_{,j k l} H^{j k l} \quad (C-7)$$

where repeated Cartesian indices are understood to be summed.

As is well known, the solution of C-5 is any functional of the constants of the motion,  $C_{(i)}(\underline{x}, \underline{v})$ , defined by

$$\left\{ C_{(i)}, H \right\}_{P.B.}^{(i)} = 0 \quad (C-8)$$

one of which is the Hamiltonian function itself. For simplicity, we shall assume that  $F_0$  is a function only of the Hamiltonian:

$$F_0 = F_0(H) \quad (C-9)$$

The generalization of the method to cases where  $F_0$  depends on other constants of the motion as well should be apparent from the ensuing development.

From (C-9) it follows that

$$F_{,j} = \dot{F}_0 H_j \quad (C-10)$$

$$F_{,j k} = \ddot{F}_0 H_j H_k + \dot{F}_0 H_{j k} \quad (C-11)$$

$$F_{,j k l} = \dddot{F}_0 H_j H_k H_l + \ddot{F}_0 (H_j H_{k l} + H_k H_{j l} + H_l H_{j k}) + \dot{F}_0 H_{j k l} \quad (C-12)$$

where

$$\dot{F}_0 \equiv \frac{dF_0}{dH} \quad \text{etc.} \quad (C-13)$$

Using C-10 and C-11, C-6 becomes

$$\frac{1}{m} (1 - \Downarrow) F_{,j} H^j = \frac{i}{2m^2} (1 - \Downarrow) (\ddot{F}_0 H_j H_k H^{jk} + \ddot{F}_0 H_{jk} H^{jk}) \quad (C-14)$$

Since in general

$$(1 - \Downarrow) A_{ijh\dots}^{ijh\dots} = 0 \quad (C-15)$$

C-14 becomes simply

$$\frac{1}{m} (1 - \Downarrow) F_{,j} H^j = \frac{i \ddot{F}_0}{2m^2} (1 - \Downarrow) \left[ (H_k H^k)^j H_j \right] \quad (C-16)$$

Making use of the identity

$$\frac{1}{m} (1 - \Downarrow) (A(H) B)_{,j} H^j = \frac{A(H)}{m} (1 - \Downarrow) B_{,j} H^j \quad (C-17)$$

the solution of C-16 is immediately obtained:

$$F_{,j} = \frac{-i}{2m} \ddot{F}_0 H_k H^k \quad (C-18)$$

Inserting this result into C-7 and making extensive use of C-15 leads after some straightforward algebra to the  $F_2$  equation

$$\begin{aligned} \frac{1}{m} (1 - \Downarrow) F_{2,j} H^j &= \frac{\ddot{F}_0}{4m^3} (1 - \Downarrow) H_j (H_{kl} H^{kl})^j \\ &+ \frac{\ddot{F}_0}{6m^3} (1 - \Downarrow) H_j (H_k H_l H^{kl} + H_k H_l^k H^l \\ &\quad + H^k H^l H_{kl})^j \\ &+ \frac{\ddot{F}_0}{8m^3} (1 - \Downarrow) H_j (H_k H_l H^k H^l)^j \end{aligned} \quad (C-19)$$



which is immediately solved using C-17:

$$F_2 = -\frac{\ddot{F}_0}{4m^2} (H_{kl} H^{kl}) - \frac{\ddot{F}_0}{6m^2} (H_k H_l H^{kl} + H_k H_l^k H^l + H^k H^l H_{kl}) \\ - \frac{\ddot{F}_0}{8m^2} (H^k H^l H_k H_l) \quad (C-20)$$

The general method for obtaining  $F_n$  should now be clear. One simply manipulates the right hand side of its equation into a sum of terms each of which is of the form of a derivative of  $F_0$  times the Poisson Bracket of the Hamiltonian with a scalar formed from tensor products of the Hamiltonian. In view of the regular structure of C-18 and C-20, it is no doubt possible to write down a simple general solution for any  $F_n$ . Indeed, it is apparent from these results that

$$F_n = \left(\frac{i}{m}\right)^n \frac{1}{n!} \sum_{p=2}^{2n} a_p \frac{d^p F_0}{dH^p} \times (\text{scalar formed from } p \text{ H's}) \quad (C-21)$$

but we have not pursued this line of investigation.

To apply the foregoing results to the problem formulated in Chapter V, we let  $H$  be the Hamiltonian

$$H = \frac{1}{2} m v^2 + U(r) - \frac{2\pi e^2 \hbar^2}{m^2} \int \frac{F(r, r')}{|r - r'|^2} d^3 r' \quad (C-22)$$

Expanding it in powers of  $\hbar$ ,

$$H \equiv \sum_{n=0}^{\infty} \hbar^n H_n \quad (C-23)$$

we have

$$H_0 = \frac{1}{2} m v^2 + U(r)$$

$$H_2 = -\frac{2\pi e^2}{m^2} \int \frac{F_0(r, v') d^3 v'}{|x - x'|^2} \quad (C-24)$$

Then, to order  $\hbar^2$ , there follows

$$\begin{aligned} F^{(2)} = & F_0(H_0) - \dot{F}_0(H_0) \frac{2\pi e^2 \hbar^2}{m^2} \int \frac{F_0(H_0(r, v')) d^3 v'}{|v - v'|^2} - \frac{i\hbar}{2m} \ddot{F}_0(H_0) H_{0k} H_0^k \\ & - \frac{\hbar^2}{4m} \ddot{F}_0(H_0) H_{0kl} H_0^{kl} - \frac{\hbar^2}{6m^2} \ddot{F}_0(H_0) [H_{0k} H_{0l} H_0^{kl} + H_{0k} H_0^k H_{0l} \\ & + H_0^k H_0^l H_{0kl}] - \frac{\hbar^2}{8m^2} \ddot{F}_0(H_0) [H_0^k H_0^l H_{0k} H_{0l}] \end{aligned}$$

(C-25)

The derivatives of  $H$  are particularly simple in the present example and the result quoted in the text follows trivially from C-25.